Tyco Laboratories, Inc.
Bear Hill
Waltham, Massachusetts 02154

ANOMALOUS WATER

First Semiannual Technical Report

ARPA Order No.:	1463	Contract No.:	DAAH01-71-C-1216
Program Code No.:	OD10	Principal Investigator: and Phone No.:	Dr. S. B. Brummer 617 890-2400
Name of Contractor:	Tyco Laboratories, Inc.	Scientist: and Phone No.:	Dr. S. B. Brummer 617 890-2400
Effective Date of Contract:	June 1, 1971	Short Title of Work:	Anomalous Water
Contract Expiration Date:	May 31, 1972	Amount of Contract:	$85,306

Sponsored By

Advanced Research Projects Agency
ARPA Order No. 1463

This report was supported by the Advanced Research Projects Agency of the Department of Defense and was monitored by ~~Air Force Cambridge Research Laboratories~~ under Contract No. DAAH01-71-C-1216.
ARMY MISSILE COMMAND

Unclassified
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Tyco Laboratories, Inc. Bear Hill Rd. Waltham, Massachusetts. 02154	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

Anomalous Water

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
First Semiannual Technical Report 1 June 1971 - 30 November 1971

5. AUTHOR(S) (First name, middle initial, last name)
S.B. Brummer
J.I. Bradspies
G. Entine
E. Trickett
H. Lingertat

6. REPORT DATE January 1972	7a. TOTAL NO. OF PAGES ~~54~~ 63	7b. NO. OF REFS 28
8a. CONTRACT OR GRANT NO. DAAH01-71-C-1216 b. PROJECT NO. ARPA Order No. 1463 c. Program Code No. OD10 d.	9a. ORIGINATOR'S REPORT NUMBER(S) C167 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	

10. DISTRIBUTION STATEMENT
This report was supported by the Advance Research Projects Agency of the Department of Defense and was monitored by [redacted] under Contract No. DAAH01-71-C-1216.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY U.S. Army Missile Command Redstone Arsenal Alabama 35809

about

13. ABSTRACT
Experiments are reported on the preparation and characterization of anomalous water. Preparations are reported with various glass substrates drawn into the form of cones. Zirconia-based glass yields the purest "polywater" infrared spectrum and, in particular, the frequently observed band at $\sim 1100/cm^{-1}$ is not present. Data presented suggest that anomalous water is formed when glass reacts with certain (unidentified) air-borne organic compounds. The final product appears to be the salt of an organic acid. Mass spectroscopy suggests a molecular weight of 207 for the most thermally stable component of this material. Refractive index data show that the material is similar to that produced in the U.S.S.R., and distillation-decomposition experiments argue strongly that none of their material is polymerized water. There are still some significant differences, however. Experiments to resolve these differences are suggested.

DD FORM 1 NOV 65 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

Unclassified
Security Classification

Unclassified
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
cone						
quartz						
Pyrex						
zirconia						
infrared spectrum						
AgBr						
sodium tetraborate						
extraction						
condensation						
distillation						
residue						
decomposition						
carboxylic acid						
mass spectroscopy						
molecular weight						
mass number						
D_2O						
refractive index						
capillary						
lens						
focal length						

Unclassified
Security Classification

Tyco Laboratories, Inc.
Bear Hill
Waltham, Massachusetts 02154

ANOMALOUS WATER

First Semiannual Technical Report

Contract No. DAAH01-71-C-1216

1 June 1971 -- 30 November 1971

Prepared For

Department of the Army
U.S. Army Missile Command (ARPA)
Redstone Arsenal
Alabama 35809

ABSTRACT

Experiments are reported on the preparation and characterization of anomalous water. Preparations are reported with various glass substrates drawn into the form of cones. Zirconia-based glass yields the purest "polywater" infrared spectrum and, in particular, the frequently observed band at $\sim 1100\ cm^{-1}$ is not present. Data presented suggest that anomalous water is formed when glass reacts with certain (unidentified) air-borne organic compounds. The final product appears to be the salt of an organic acid. Mass spectroscopy suggests a molecular weight of 207 for the most thermally stable component of this material. Refractive index data show that the material is similar to that produced in the U.S.S.R., and distillation-decomposition experiments argue strongly that none of their material is polymerized water. There are still some significant differences, however. Experiments to resolve these differences are suggested.

Table of Contents

List of Illustrations

List of Illustrations (Cont)

List of Tables

I. INTRODUCTION

"Anomalous water" was the name given by Fedyakin[1] to the fluid which condenses inside fine capillaries in presence of undersaturated H_2O vapor. This material has been extensively investigated by Deryagin and his coworkers [see for example references (2) and (3)]. From this work, it has been shown that anomalous water is a solution of a residue in H_2O. The residue solidifies at -40°C, distills at 300°C,[2] has a density of 1.4,[4] a refractive index of 1.49,[5] a molecular weight of 180 ± 50,[6] and raises the surface tension of water when dissolved.[7] It decomposes back to water on excessive heating.[2,3,8] Some of these properties have been explored by Western workers and, specifically, the freezing behavior,[9,10,11] and the refractive index[12,13] have been verified.

In addition, the residue has been chemically analyzed[13,14,15] and its infrared spectrum has been determined.[13,14,16] In their work on the IR spectrum and the chemical analysis of the residue, Lippincott, et al.,[13] found the virtual absence of all significant impurities except for variable amounts of Na (<0.5%) and obtained a "unique" infrared spectrum. They also reported on the Raman spectrum. From these data, they concluded that the residue is a polymer of water. In agreement with conclusions in the Russian literature,[3] they called the material "polywater."

Rousseau and Porto[14] undertook studies similar to those of Lippincott, et al. They confirmed the infrared spectrum, concluded that the Raman spectrum was in error, and found relatively large concentrations of inorganic salts in their samples. While the latter could not account for the infrared spectrum, it was inferred tentatively that "polywater" was unlikely to be a polymer of water. Subsequently,[17] it was suggested that the "unique" infrared spectrum of "polywater" could be duplicated by trivalent formates and acetates (see, also, ref. 26). This model was not satisfactory, however, because of the difficulty of understanding how these unusual materials could have been introduced into the material. In further work,[18,19] it

was suggested that the infrared-active component of "polywater" derives from a human sweat aerosol present in the laboratory air which deposits on the surface of the glass. The infrared-active component was claimed to be sodium lactate.[18] In support of this hypothesis were analytical data involving electronic spectra and mass spectra.[20] The former showed the presence of carboxylic acid groupings in U.S. prepared material; the latter indicated the presence of phospholipids in USSR prepared material.

This conclusion that "polywater" is a conglomeration of inorganic and infrared-active organic compounds could not, in our view, account for all the reported properties of the material. For example the surface tension of anomalous water,[7] its decomposition properties,[8] its volatility,[2,3] and the reported absence of organic material in some samples[20] pose problems. In addition, some workers[2,20,21,22] report forming the material under organic-free conditions.

It is clear then that a considerable controversy exists over the possible identity of "polywater." The recent report[17] that "polyheavywater" has a similar spectrum to "polywater" argues strongly against a polymerized water model. However, positive identification of what appears to be an interesting fluid has not been made. The difficulty in this regard relates to the very low and erratic yields of material which have been reported by the various workers. For example, Willis, et al.,[9] report that 5-10% of their capillaries contained product. Others[14,15] have also reported poor and irreproducible material preparation. The only prior report of substantial material production was by Page, et al.,[23] who claimed that milligram size quantities of "polywater" had been produced in large quartz tubing. Preliminary results with this material indicated, however, that it was highly contaminated, containing up to 12% C.

Our work with anomalous water has had two objectives:

1. To produce enough material to verify its chemical composition unequivocally.

2. If appropriate, to examine methods for mass-production of the material to determine its technological usefulness.

In the course of this work, most of our effort has been directed towards item (1). In doing this, it was found necessary to develop a new preparation technique (our so-called "cone method"), and extensive studies relevant to item (2)

have been made. As will appear, our present view is that most of the properties of anomalous water can be accounted for in terms of a very stable organic compound formed when glass is heated in air. We are actively seeking the identity of this compound, since we believe it may itself have some technological significance (it can withstand heating in air at 300 °C for at least 24 hr). The methods we have developed for scaleup (albeit only modest) should, then, be useful if we cannot synthesize this material using conventional organic chemical procedures.

This project has been carried out in conjunction with a contract (14-01-0001-2259) with The Office of Saline Water (OSW) of The Department of the Interior. Much of the material characterization was done on that program. Specifically, infrared spectra (to compare with U.S.-grown polywater), molecular weights (to compare with Deryagin's material), thermal stabilities, comparisons with various organic species and D_2O (to test Rousseau's sweat theory) were carried out on that program.[24]

On the other hand, all the preparative methods were developed on this program. In addition, some crucial techniques were developed and used on this program. Thus, a distillation-decomposition method has been used extensively to try to pin down one of the last remaining properties of anomalous water reported by Deryagin which still suggests that it is a polymer of water (Section IV). Also, a technique for measuring the refractive index of our samples has been developed (Section V) to make really rigorous comparisons with the Russian material. Further experiments on material preparation are also reported (Sections II and III); they confirm the organic origin of the material. Mass spectrometric studies of our material, carried out in conjunction with Dr. David Dolphin of Harvard University, and intended to identify these organic species are reported in Section V. Our present views and plans for further work are presented in Section VI.

II. PREPARATIONS OF ANOMALOUS WATER ON VARIOUS SURFACES

Although the bulk of the preparative work has utilized quartz and Pyrex, much effort has continued on examining other substrates for the formation of anomalous water. This line of investigation was prompted mainly by the observation that yield of material is much greater for Pyrex than quartz.

Consequently, various soft glasses were tested as substrates. Initial results with borosilicate glass (Corning 7052) and soda-lime glass (Corning 0080) were presented in our report of May 1971.[25] Both of these glasses produce essentially the same amount of product as Pyrex. Infrared spectra of the material from the soda-lime glass showed the usual anomalous water peaks and no sodium borate. The absorption in the region of 1400 cm^{-1} was reinforced by a carbonate peak which could be verified by its companion peak at 880 cm^{-1}. Three μg of 0.1N HCl was added to the sample to convert the carbonate to CO_2 gas. The resulting sample had a spectrum which more closely resembled that of anomalous water (Fig. 1). The presence of carbonate is best explained by the absorption of CO_2 from the atmosphere into a liquid condensate which must be basic in pH. Since the cone technique had been employed, there was undoubtedly some caustic material released from the bulk of the tubing when this tubing was melted into cones. The infrared spectrum of the borosilicate product resembled that of anomalous water but was considerably more ambiguous (Fig. 2).

Pursuing this line of approach further, we have used zirconia glass (Corning no. 7280, 15% ZrO_2, 11% Na_2O, 73% SiO_2) to form cones. This glass was selected because it contains no borates. Although its high coefficient of expansion led to difficulties in drawing cones without shattering the tubing, enough cones were made to determine the yield and the IR spectrum of the product. The yields were similar to those found in the normal Pyrex cones, while the IR spectrum is almost identical to the classical anomalous water spectrum (Fig. 3). No borate was evident, as

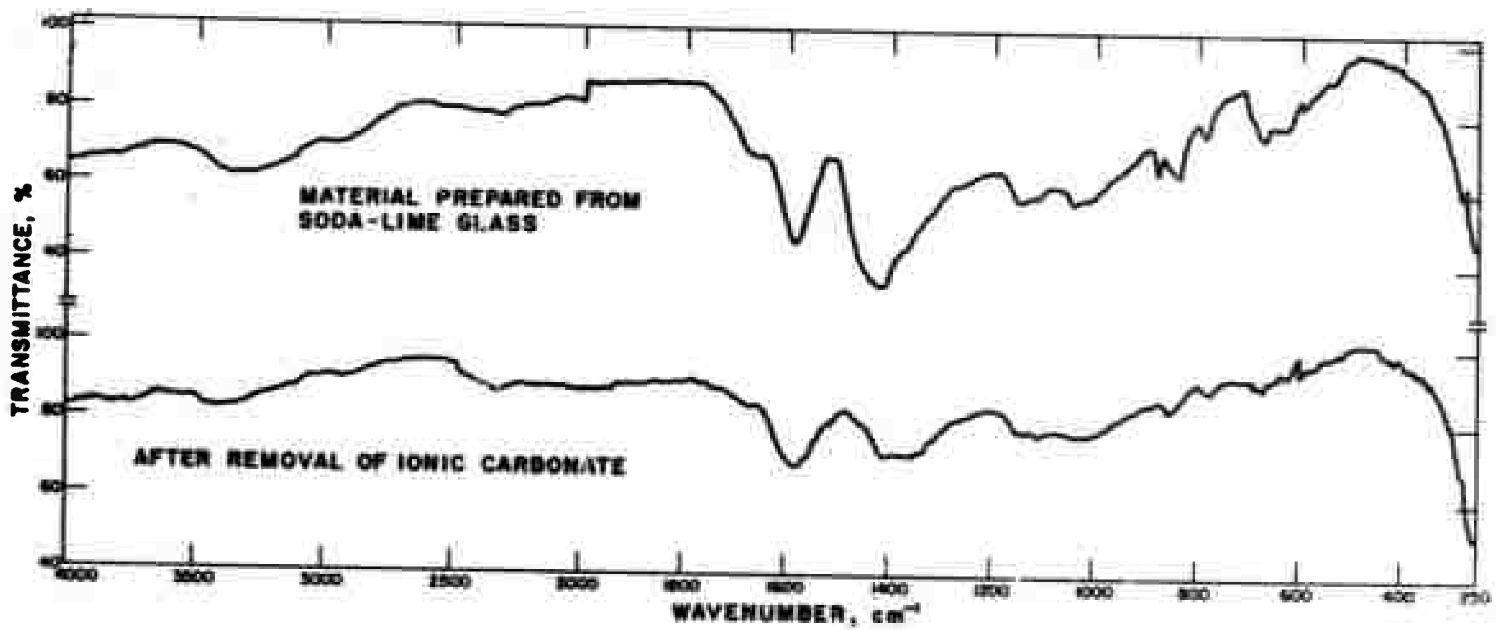


Fig. 1. IR spectrum of material produced from soda-lime glass cones

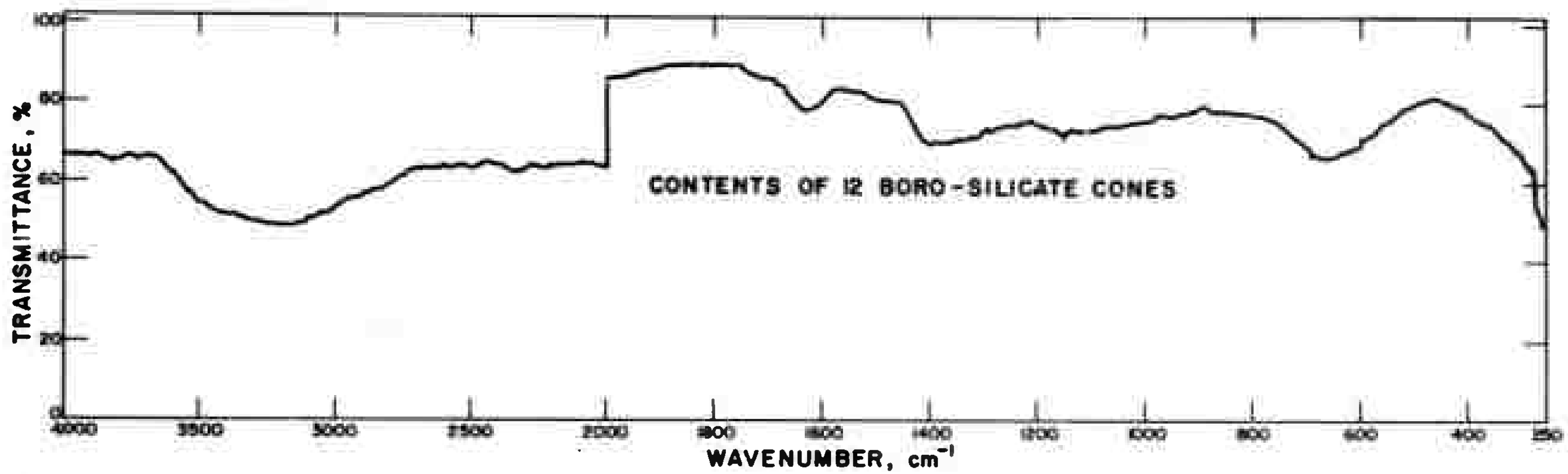


Fig. 2. IR spectrum of material from borosilicate glass cones

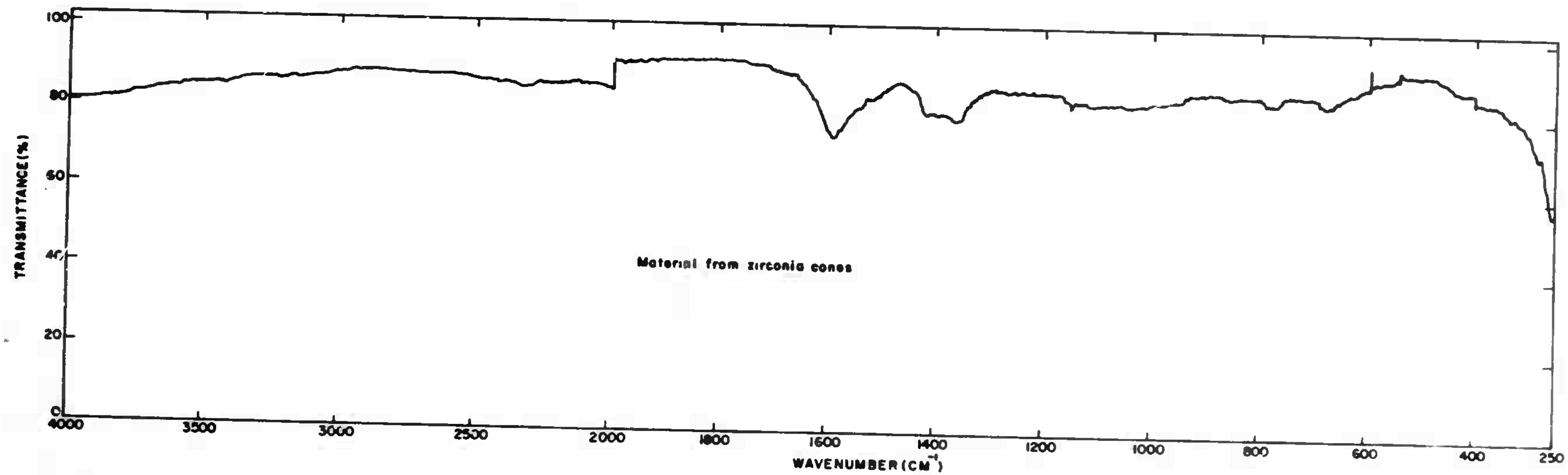


Fig. 3. IR spectrum of material from zirconia glass cones

expected. The material formed is probably of organic origin since acidifying with $1 \mu \ell$ of 0.1N HCl caused the bulk of the spectrum to disappear. This is expected for an organic acid in so far as these acids are much more volatile than their salts. However, complete identification can only be made by observing the characteristic peak shift in the spectrum after acidification; this spectrum was too weak to allow this.

To date, this is the only substrate to produce polywater which does not exhibit absorption peaks at 1100 cm^{-1}. This would indicate that absorption occurring at ~1100 cm^{-1} is not attributable to polywater but to a different compound. This spectrum has been obtained repeatedly for zirconia-grown samples.

In general, infrared analysis is somewhat limited as to the extent of chemical identification possible. However, in some cases, positive identification has been made, e.g., $CO_3^{=}$ in the soda-lime preparation and $B_4O_7^{=}$ in some Pyrex-grown samples (refer to Fig. 14, ARPA Final Report, May 1971).[25] Additional information can also be inferred by comparing the IR spectra for zirconia-grown and quartz-grown material (Fig. 4). It is immediately obvious that the main difference is that there is considerably absorption in the 1100 cm^{-1} region for the quartz-grown sample. It would be difficult to attribute the contaminant to the environs of the substrate since the preparative techniques were the same and both spectra have been reproduced many times. It is more likely that the source of contamination is the substrate itself and is therefore a silicate. This hypothesis is further substantiated by the fact that SiO_2 absorbs at ~1100 cm^{-1} in the infrared. It is quite possible that the high temperature required to melt quartz into cones is responsible for the deposition of a small amount of silica powder on the cone wall.

While this explanation as to the source of the 1100 cm^{-1} contaminant is only a postulate, it is felt that the lower melting zirconia glass is a more suitable substrate for the preparation of pure anomalous water. Using infrared analysis as a standard, it would appear that zirconia-grown material is the least contaminated of all tested including those from substrates reported in our previous report.[25]

It was hoped that such experiments would lead either to increased yield or to some understanding of why anomalous water is more readily produced on Pyrex than on quartz. Apparently the differences between Pyrex and quartz which affect the production of anomalous water are not influenced by the addition of more borates or the replacement of borates by soda-lime or ZrO_2. This finding suggests that the temperature of formation of the cone may be the determining factor in the

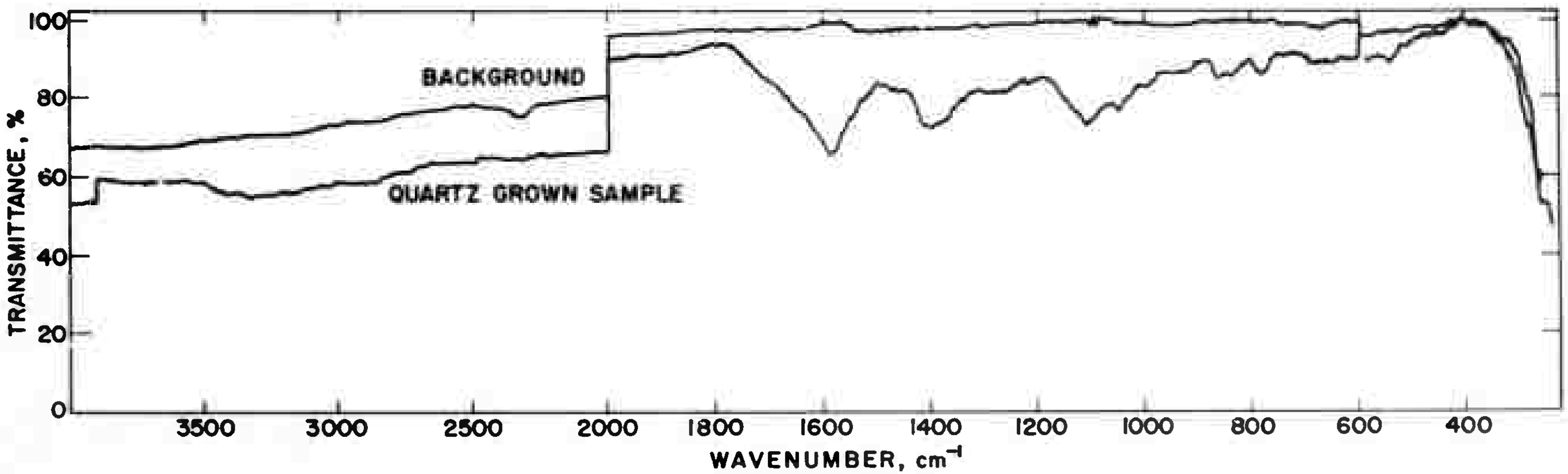


Fig. 4. IR spectrum of quartz grown polywater

process. This formation process was investigated with the zone experiment initiated in the previous report period and now complete. Tubes heated for 1 min at temperatures between 600 and 800 °C were exposed to water vapor in the usual way and examined for condensation. No condensation was formed either inside the heated zone, or in bands near the ends of the zone. It was therefore concluded that the previous hypothesis that anomalous water is formed by thermal gradients in the glass, either radial or longitudinal, is not correct.

Another experiment, which was also designed to investigate the effect of temperature on polywater formation, was performed whereby the Pyrex substrate was melted without the use of a flame. A 15-mm Pyrex tube, placed on a quartz plate was heated at 1100 °C for 1-1/2 hr and then air-cooled. After exposure in a desiccator, the product was collected and analyzed by infrared spectroscopy. The spectrum shows strong borate peaks but no anomalous water bands. The tube was then reexposed. This time, the produce showed both borate and anomalous water peaks. This result is similar to that obtained from striped cones (see previous report)[25] and its interpretation is not clear. Whether anomalous water is formed initially and is masked by the borate, or whether the borate must be first removed to activate the surface for anomalous water formation has yet to be shown. The former explanation seems more likely. In any event, it was decided to discontinue Pyrex activation by heating since attempts to separate out the borates (e.g., by washing and/or distillation) were not successful and, therefore, the primary goal of the experiments, i.e., to determine whether anomalous water yields could be increased, was not achievable.

An experiment was carried out using zirconia cones which had been annealed at 627 °C for 15 min and then cooled to 400 °C in 25 °C steps in 2 hr before oven-cooling. The yield of these cones was similar to that of the unannealed cones, in contrast to the behavior of the yield of Pyrex cones, which is significantly reduced by annealing. This may be explained, in part, by the presence of borates in many Pyrex-grown samples and the relative lack of contaminants in zirconia-grown-material. In other words, annealing Pyrex cones lowers the solubility of the glass, perhaps by conversion of tetraborate powder to fused B_2O_3.

One experiment suggested by Mr. Normal of Redstone Arsenal was designed to explore the effect of having two glass surfaces in close proximity. A watchglass was placed on a Pyrex plate and the whole assembly exposed overnight in a desiccator. Ideally, a ring of condensate would be found at a distance from the point of

contact determined by the optimum separation for the production of product. What was found was a pool of liquid 0.8 cm in diameter. This diameter was determined by the amount of water absorbed by the polywater and therefore cannot be directly related to the optimum glass surface separation. The infrared spectrum of the material, although quite weak, displays three peaks of roughly equal intensity, at 1100, 1400, and 1600 cm^{-1}. Such a spectrum is more similar to the Battelle "blank"[23] than to anomalous water. The quantity of material produced was about 3 μg per watch-glass.

We conclude, from these experiments, that the only promising approach to anomalous water production is the basic cone method, selecting a glass substrate which allows minimum contamination. It is our opinion that the cone method minimizes manipulation and handling of the glass, thereby reducing possible sources of contamination, as well as being efficient in terms of the amount of product per unit of labor.

III. THE ORIGIN OF POLYWATER

As has been indicated, there is considerable controversy over the identity of anomalous water. Originally, Lippincott, et al.,[13] reported a unique infrared spectrum and a low impurity level for the involatile residue, which they called polywater. While this spectrum has been reproduced, many workers have found high levels of impurities, among them being acetates detected by Rousseau,[17] borates detected by Rabideau,[15] and the most recent, sodium lactate by Rousseau.[18, 19] Sodium lactate is the infrared active component of human sweat which, Rousseau claims, precipitates on a quartz surface to form a material which is responsible for the infrared spectrum of polywater. Our own data have directly confirmed organic constituents in some polywater samples by the presence of C-H stretching peaks in IR spectra.

Ultimately, to prove or disprove any one of the many adventitous impurity theories, chemical analysis must be carried out. In addition, this theory that polywater is a conglomeration of inorganic and infrared-active organic compounds must also be compatible with the reported properties of the material, i.e., its decomposition properties and its volatility.[2, 3]

An experiment has been performed to investigate the hypothesis that an organic aerosol, possibly arising from human sweat, is the source of the infrared-active component of anomalous water. In particular, it was hypothesized that airborne organics deposit on the hot glass of the cones during the pulling process. Simply, this experiment is based on the premise that if the interior of the tubing to be drawn into cones is not exposed to the atmosphere at any time during the coning process, then the primary source of such organic contamination will be eliminated. Observing the yield and infrared spectrum of material prepared under this condition should be most revealing. The details of this experiment were as follows: A long section of Pyrex tubing (sufficient for six cones) was cleaned with HNO_3 in the usual

manner. Then, it was attached to a vacuum system in which only Teflon and glass were used between the tubing and a cold trap. After vacuum drying, the tube was back flushed with purified oxygen and while being flushed, it was baked in a furnace at 300°C for 2-3 hr. The furnace was then removed, and the tube drawn into double cones with a C_3H_8-O_2 torch. After cooling, these double cones were cut and the resulting single cones exposed as per usual. The yield was determined to be 1.2 μg/cone, which is somewhat lower than the yield from normal Pyrex cones (average ~ 2μg/cone).

Subsequently, the material was characterized under the OSW program. The initial test to be performed was infrared analysis (Fig. 5). One immediately observes that the 1600 cm^{-1} peak, usually present in polywater spectra, is entirely missing. It would appear, in this case, that the only IR-active component of the sample is tetraborate. In order to explore this further, the molecular weight was determined. It was found to be 117. To complete the comparison, the molecular weight was also determined (using, for consistency, the density for polywater in the calculation) for $Na_2B_4O_7$. This proved to be 75. It is clear, then, that the material obtained from clean cones is not pure tetraborate but a molecular weight of 117 is considerably lower than that observed for any Pyrex-grown polywater (average 183 ± 35). The drying behavior of the two materials also suggests they are dissimilar, since the tetraborate crystallizes out while the polywater tends to gel.

In order to confirm this unique IR spectrum and to avoid the possibility that the baking at 300°C was responsible for the different spectrum, a control experiment was performed. The original preparation was repeated but with the difference that after baking in O_2 at 300°C the tube was cooled and then <u>exposed to the atmosphere.</u> It was left exposed while being flamed into cones. These cones were then exposed to water vapor, exactly as usual, and the material infrared analyzed. The spectrum displayed a strong absorption peak at 1600 cm^{-1}, as is usual for polywater. There can be no doubt then that the source of this peak is the atmosphere. The rest of the spectrum was also typical of polywater.

We feel that this is strong evidence in support of the theory that the source of polywater (or at least its infrared active component) is the result of the decomposition of air-borne organics on hot glass.

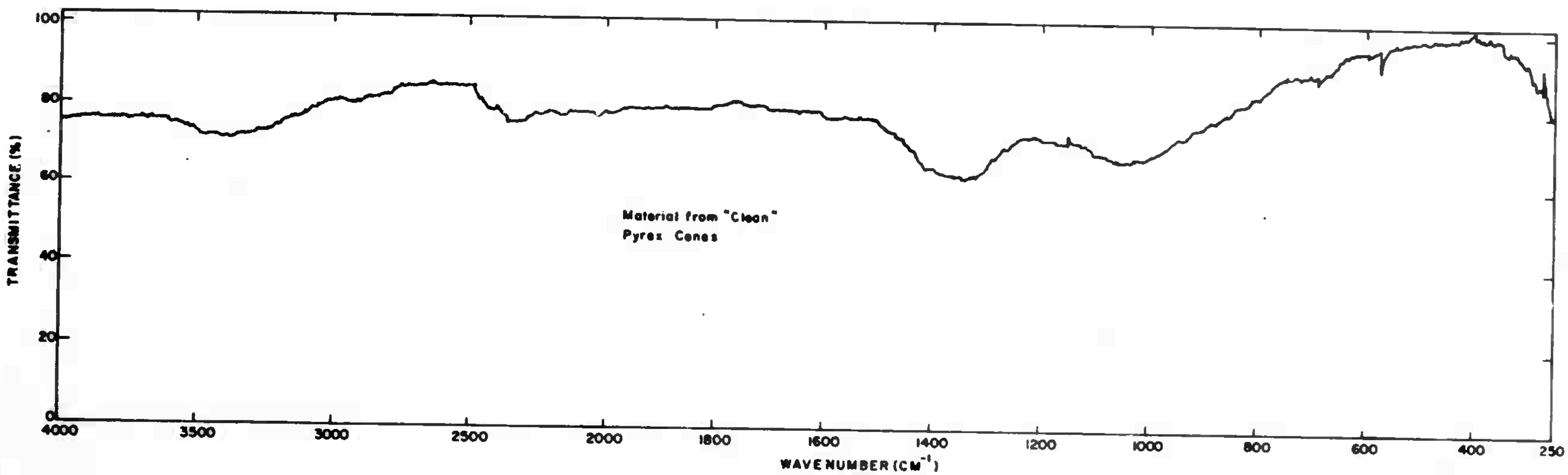


Fig. 5. IR spectrum of material from clean Pyrex cones

A complementary experiment to the above was carried out under the OSW program and involved deliberately contaminating Pyrex cones with sweat. After a set of Pyrex cones was prepared, 10-20 μl of a solution of sweat was placed in each cone and the cones were then "reflamed". The normal coning procedure involves reflaming them after their original drawing, to reshape the cone. The approximate temperature achieved during this procedure is 1100°C, which is sufficient for softening and working Pyrex, and which is also far in excess of the temperature required to decompose sodium lactate. The cones were allowed to cool and then immediately extracted with liquid H_2O. The aim here was to eliminate the glass-water vapor interactions which have been postulated to be the primary driving force for the formation of polywater. The extraction was accomplished by placing ~0.5 ml of distilled water directly into the cone tip, siphoning it out, placing it into the next cone, and so forth. In this way, it was felt that the material extracted would be restricted to the decomposition product of the sweat during the reflaming of the cones. After completing the extraction, an aliquot of the solution (~1% of the total volume) was mounted on an AgBr plate and allowed to desiccate for infrared analysis.

Fig. 6 shows the resultant spectrum. No attempt had been made to separate out salts from the sweat solution, which were undoubtedly present in substantial concentrations. The IR spectrum reflects this, with very strong ionic sulfate peaks at 1100 and 620 cm^{-1}. Also evident in this spectrum are peaks at 1630 and 1400 cm^{-1} which, while typifying polywater, are in this case due to the decomposition product of the sweat. The presence of a carbonate, which absorbs at 1430 cm^{-1}, is highly improbable since there is no indication of its companion peak at 800 cm^{-1}.

These results are quite significant since they clearly demonstrate than an organic contaminant (such as sodium lactate), once introduced onto a hot glass surface, does not necessarily experience complete combustion but rather may decompose to a compound which is still infrared active. This experiment was repeated for the purpose of extending it to include a distillation of the extracted material. If in fact there is a distillation product, a comparison of its IR spectrum with those of other polywater distillates could be helpful in assigning an identity to the material. Distillation would also serve to separate the organic constituents from the inorganic salts which are present in heavy concentrations in sweat.

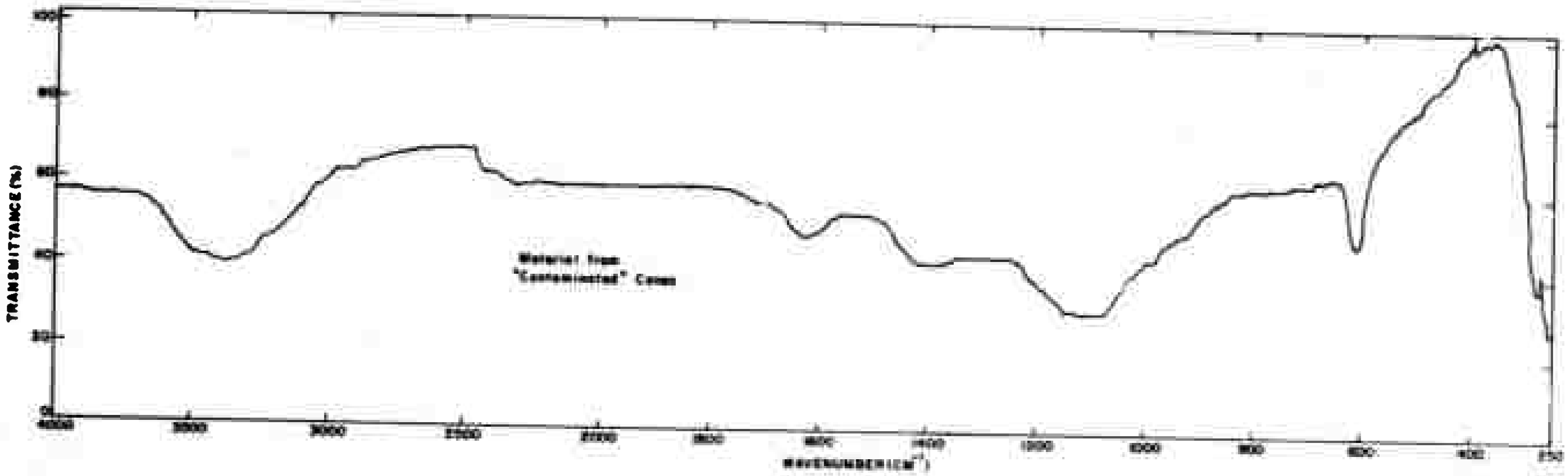


Fig. 6. IR spectrum of material from sweat contaminated cones

The technique employed for the distillation is described in detail in Section V. It is sufficient to say here that the material was distilled under vacuum at 300 °C. A yellow oil was obtained which was not soluble in water. This fact alone denies any close relationship to polywater. The distillate was dissolved in a mixture of 75% H_2O-25% C_2H_5OH and mounted on AgBr for infrared analysis. The spectrum proved to be quite similar to that of the material prior to distillation (Fig. 7) with the exception that the 1100 cm^{-1} and 620 cm^{-1} peaks are now absent. This was anticipated since $SO_4^{=}$ was not expected to distill under these conditions.

These results indicate that it is possible to obtain an IR spectrum which is a reasonable fascimile of that of polywater from the partial decomposition of a common biological material, i.e., sweat. However, experimentation performed under the OSW program indicates that polywater is more thermally stable than sweat. This discrepancy in properties, in conjunction with the observation that the sweat distillate is a yellow oil, led us to conclude that while there may be a relationship, the two materials are not exactly the same.

In another set of experiments, we have sought to explore the sweat theory of the origin of anomalous water by washing out drawn Pyrex cones and comparing the amount of the "blank" with the amount of material formed in a normal, high humidity exposure. For this purpose, fresh Pyrex cones were filled with distilled water and left in a desiccator for 2 days. The water was then evaporated by vacuum so that the residue remained in the cones. The cones were then reexposed for 1 hr and the product collected. The material gave a spectrum more similar to Battelle's "blank"[23] than to the usual Pyrex-formed anomalous water spectrum (Fig. 8), although the quantity of material formed in each case was the same as that produced using the usual technique (~2 μg/15-mm-o.d. cone).

Evidently the small volume of condensed water formed in the normal anomalous water production procedure reacts differently with the glass than does a large volume of liquid water. This could result from extraction of material from the glass. It is claimed in the Russian literature that no comparable product to anomalous water can be leached from glass capillaries.[26] Our present data indicate that they ought to have seen material, which they would have found difficult to distinguish from their main material of interest. The different temperature-time relations achieved in cooling (their) fine capillaries might be an important difference here, however.

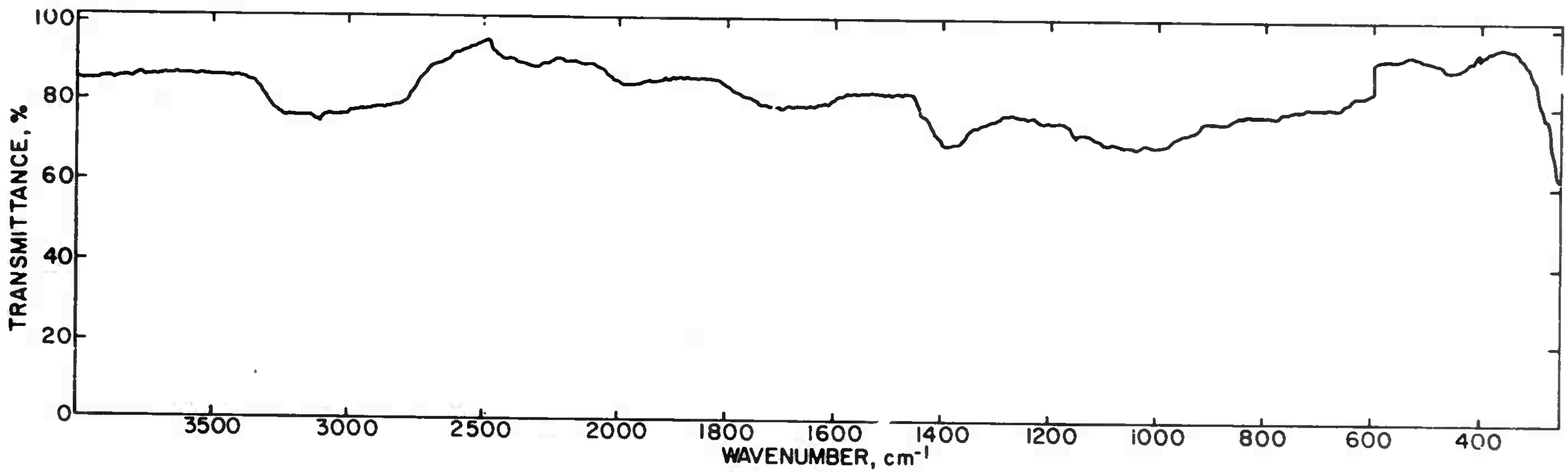


Fig. 7. IR spectrum of material obtained by distilling material from sweat contaminated cones

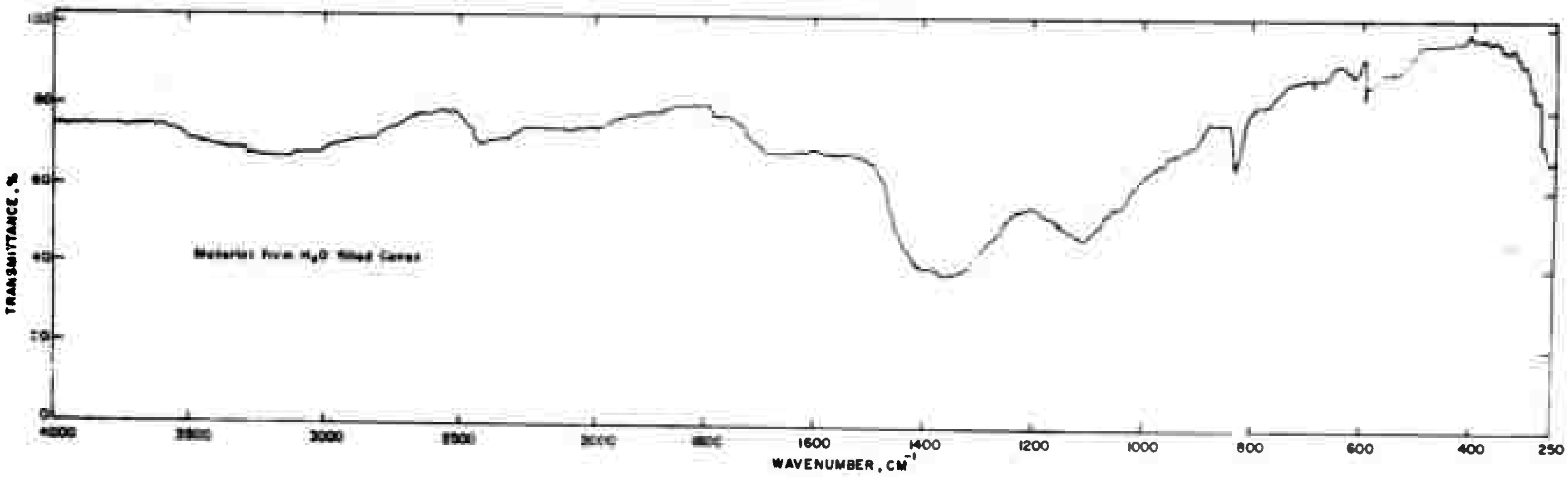


Fig. 8. IR spectrum of material from water filled cones

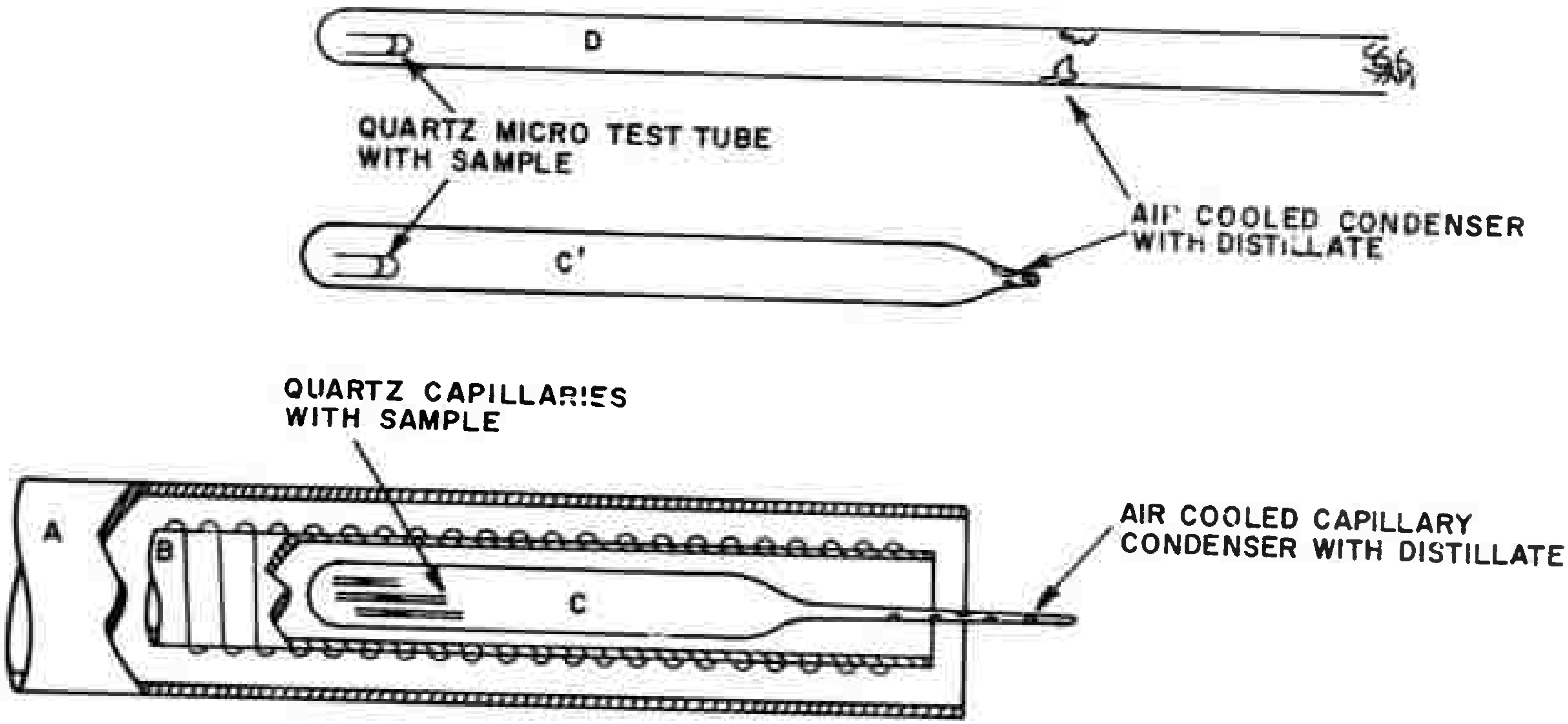
In summary, in this regard, we emphasize that there is a similar yield of product from washing heated glass as there is from exposing it, unwashed after heating, to high humidity. The identities of the products are different, however. This result argues against a simple sweat theory. It is clear though, that our data on the behavior of the IR spectrum of "polywater" with respect to heat and acidification show that it does indeed result from organic contamination.

IV. DISTILLATION OF POLYWATER

The presence of some organic material in various polywater samples prepared in this laboratory has been confirmed by infrared analysis. Indeed, a substantial part of the work in the United States has focused on the infrared spectrum of polywater. The Russian work, on the other hand, has involved no IR analysis and consequently one cannot in all fairness conclude that the two bodies of work are on the same material. It is possible that only a minor component of the material which we characteristically make is in fact responsible for the various physiochemical properties observed by the Rissians. Consequently, the distillation of polywater has become a pivotal experiment serving a dual propose: (1) to link our data with that of the Russians, and (2) to purify our material.

The apparatus for distillation of polywater is shown schematically in Fig. 9. Quartz tube A (18-mm i.d.) serves to insulate the heating unit from drafts in the room and to keep the temperature constant. Tube B is a heating unit wound with Kanthal high resistance wire. The temperature (range from 50 to 800°C) of this unit is controlled by two variacs. The distillation chamber, C, is a sealed quartz tube (2.5-mm i.d., 5-mm o.d.) With one end drawn into capillary. This end is suspended outside of the heating unit and serves as an air cooled condenser. The samples to be distilled are placed in capillaries at the other end of the chamber. While being heated, the samples evaporate, escape from these capillaries, and settle at the cool end of the chamber. Tube C' is a modified distillation chamber. The capillary condenser was replaced by a cone, and any condensation at the tip of the cone can be recovered easily with a micropipet. In this case, the sample holder is a micro-test tube, which is much more easily handled than the capillaries. Tube D was for distillation experiments being done at atmospheric pressure (e.g., $Na_2B_4O_7$).

In all, seven distillations of polywater, plus attempts to distill $Na_2B_4O_7$ and poly D_2O_1 have been carried out to date. The results are summarized below:



A. QUARTZ INSULATION TUBE, 18 m.m. i.d.

B. HEATING UNIT, 7 m.m. i.d.

C,C',D. DISTILLATION CHAMBER, 2.5 m.m. i.d., 5 m.m. o.d.

Fig. 9. Distillation apparatus

Distillation no. 1: A sample of polywater collected from Pyrex cones was transferred into capillaries, dried, and placed in distillation chamber C. The distillation chamber was evacuated (to about 0.5 mm Hg pressure) and sealed under vacuum. The sample was heated initially at 100°C, and no condensation was observed at the tip of the capillary condenser. The temperature was then increased gradually, while the distillation chamber was observed very carefully with the help of a microscope. No visible condensation was observed at 250°C or after 1 day at 300°C. However, a product distilled over at 300°C during the next 3 days. We purposely kept the temperature as low as possible to minimize decomposition. According to our observation, the solid-like starting material did not melt but went into the gas phase directly and condensed at the cool end. Black solid materials, which did not distill, were left inside the capillary sample holders. Because of the minute amount of the distillate, no attempt was made to identify the product directly. As an indirect test, the distillation chamber was placed in an oven and was heated to 700°C overnight in order to see if the product would decompose to normal water, as reported by Deryagin.[2, 3, 8] The distillate disappeared after heating and the distillation chamber was again placed inside the heating unit and the distillation repeated. However, no condensation was observed. It seems that the decomposition product of the distillate must have reacted with the hot quartz and it was not possible to identify it.

Distillation no. 2: This distillation was done with distillation chamber D. To remove organics, the distillation chamber was baked at 200°C in the presence of air for 2 hr and the sample (about 100 μg) was heated at 200°C in air for 2 hr before use. Otherwise, the procedure and handling were the same as described above. After 2 days at 300°C, some crystalline material was found at the tip of the cone. The distillation was completed, after 5 days, i.e., there was no more increase in product formation. The chamber was opened and the distillate was exposed to water, the solution was transferred to an AgBr plate. While the IR spectrum of this product is weak (Fig. 10), it shows absorption at 1580, 1380, and 1080 cm^{-1} (characteristic of polywater), and a very weak band at 1700 cm^{-1} (characteristic of carboxylic acids). This sample was then deliquesced and transferred to a capillary tube and dried over P_2O_5.

When the sample was completely dried, the capillary was cut and sealed at both ends and reserved for a decomposition experiment. For this purpose, the capillary was placed in the distillation apparatus directly at 600°C. One tip of the

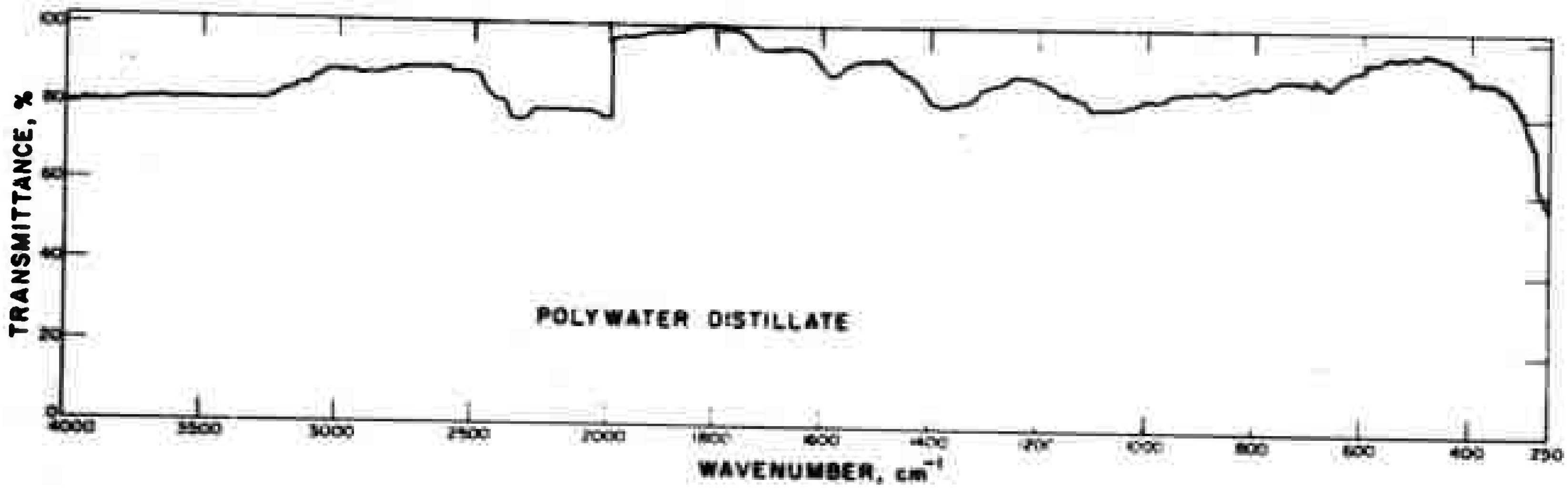


Fig. 10. IR spectrum of distillate no. 2

capillary was left outside the heating coil and, after 30 min of heating, a liquid condensate appeared at this cool end of the capillary. Condensation was complete in 4 hr.

The capillary with the decomposed product was placed into a freezing point determination cell and a control experiment was done with distilled water in a capillary tube. These two capillaries were placed side by side in the freezing cell. The cell was cooled down to -45°C with cold N_2 gas and the temperature was brought up slowly (2°C/min) and the melting process of both samples was observed. The melting point for both samples was 0°C. The result of this experiment suggests that the decomposition product was water. This water was presumably the decomposition product of a polymer of water, a similar conclusion to that shown in the Russian work.[2]

In order to ensure that this liquid condensate could not have been water previously adsorbed on the capillary walls, two control experiments were performed: (1) a 6-cm capillary was dried over P_2O_5 and sealed at both ends; the decomposition procedure was then repeated as described above, but no liquid was found at the cold tip of this capillary, and (2) another 6-cm capillary was filled with water, dried over P_2O_5, and sealed. After this capillary was heated at 600°C, no liquid condensate was observed.

One precaution which had not been taken in this preliminary experiment was to eliminate oxygen in the capillary by evacuation before sealing and heating at 600°C. If, in fact, the distillate were organic, then the presence of oxygen would have aided its oxidation to CO_2 and water. In any event, the decomposition experiment just described was not quantitative; there was a small amount of what may have been a char still remaining. A similar set of experiments was also carried out on other materials (distillation no. 5).

Distillation no. 3: A third distillation was carried out with the same apparatus. The distillation chamber was baked at 200°C in the presence of O_2 for 4 hr and the sample (about 200 μg) in a micro-test tube was dried and heated at 250°C for 8 hr before use, in order to eliminate organic materials. The sample was then placed in the distillation chamber, evacuated to less than 0.5mm Hg pressure, and sealed. Then the sample was heated at 300°C. After 1 day, a crystalline product started to form at the tip of the cone. It took 5 days to complete the distillation. The chamber was opened and the product was exposed to water vapor. The distillate deliquesced and the solution was transferred to an AgBr plate for IR measurement.

Although the IR absorption of this material is very weak, a band at 1650 cm^{-1} and a broad band at 1250-1380 cm^{-1} were observed. When this sample was acidified with dilute HCl and the IR scan repeated, the signal was considerably weakened but no shift could be observed. This may have been due to volatilization or spreading of the sample on the AgBr plate; it does seem to indicate absence of carboxylic acids, however.

The residue of the distillation was also transferred to an AgBr plate for IR measurement. The IR spectrum of this residue shows strong absorption at 3200 - 3500 cm^{-1}, broad band at 900 - 1400 cm^{-1} region, and also absorptions at 700 and 1600 cm^{-1}. This spectrum suggests that the major portion is borate.

The difference between the second distillation and the third is that the sample of the latter was baked at 250°C in the presence of O_2 for 8 hr instead of at 200°C in air for 2 hr. The conditions for cleaning the sample are very vigorous and a good portion of the material was lost during this process.

Distillation no. 4: This distillation was done with the same apparatus. The distillation chamber was baked at 200°C in O_2 for 4 hr. The pretreatment of the polywater sample, on the other hand, was altered quite drastically. It was felt that if there were salts of carboxylic acids present, then additions of acid would effect a conversion from salt to acid and result in volatilization of the material and thereby eliminate the organic constituents. Consequently dilute HCl was added to the sample, which was then heated at 100°C for 4 hr. This process was repeated. Finally the sample was neutralized with NH_4OH and distilled, as before, at 300°C. The neutralization was to ensure that any borates would be present in the form of involatile salts and not distill. The fact that only a minute amount of distillate was obtained may attest to the fact that a major portion of the starting material was organic and lost as a result of the pretreatment.

Distillation no. 5: The experimental procedure and sample treatment were identical to the distillation no. 2 with the exception of sample size; this preparation being 500 μg of Pyrex-grown material. The distillation required 1 week to complete and yielded much more distillate than in all the previous experiments. An infrared spectrum was obtained which suggests the presence of both borates and organic material (Fig. 11). A spectrum was also obtained for the undistilled portion of the sample and is shown in Fig. 12. The bulk of this residue was not water soluble (probably carbon) and was separated out before running the IR analysis. One can

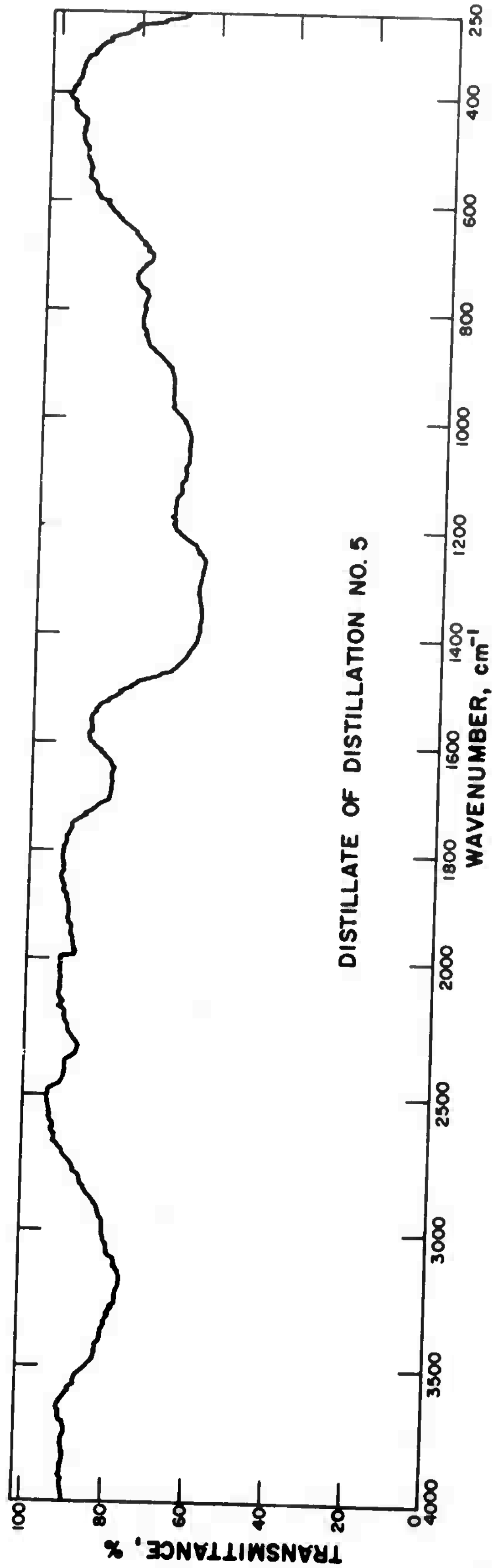


Fig. 11. IR spectrum of distillate no. 5

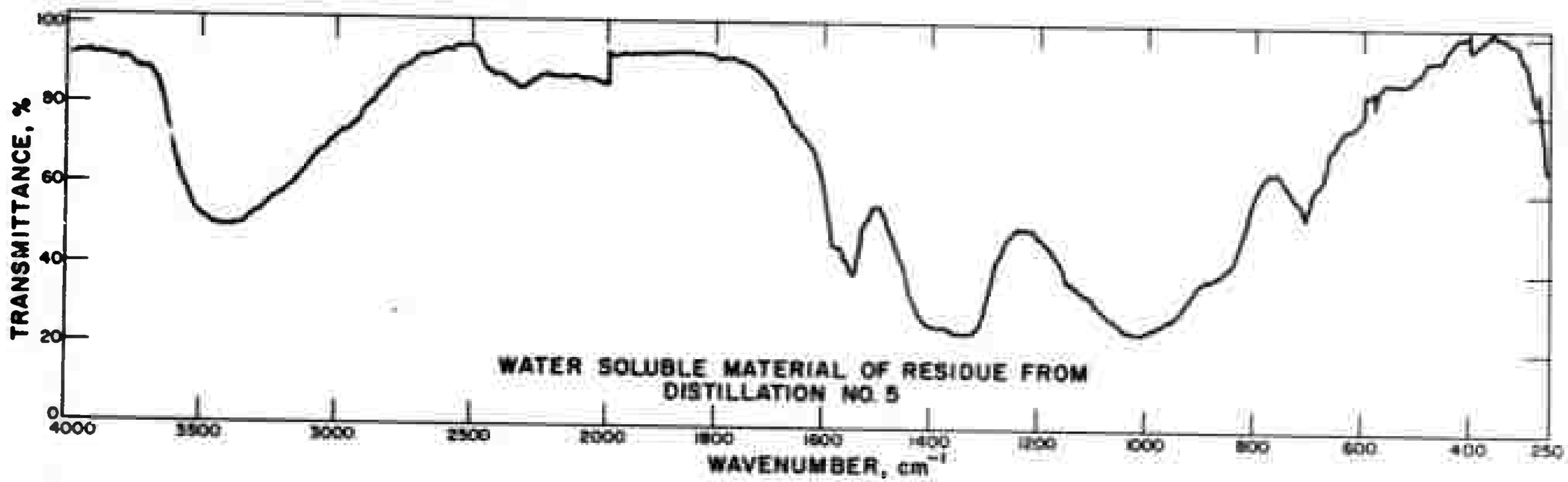


Fig. 12. IR spectrum of undistilled portion from distillation no. 5

see that the two spectra have a great deal in common, but are not conclusive. The main differences lie in a shift of the 1550 cm^{-1} peak of the residue to 1650 cm^{-1} in the distillate, plus the appearance of a peak at 1200 cm^{-1} in the distillate.

Due to the substantial yield of distillate (estimated at ~25 μg), it was possible to determine its molecular weight which was found to be 262. Since tetraborate was identified in the residue by IR analysis (see Fig. 13), it is not surprising to observe a higher molecular weight for this distillate than for previous undistilled Pyrex-grown polywater samples (average weight = 183 ± 35). The molecular weight of a mixture determined by applying Raoult's law would be the algebraic average of all components and, as was mentioned above, the molecular weight observed by this method for $Na_2B_4O_7$ was 75.

After the completion of the molecular weight determination, distillate no. 5 was divided into two aliquots for a decomposition experiment. In the presence of a sufficient quantity of O_2, organic material is most likely to decompose to H_2O and CO_2 at high temperatures. In absence of O_2, it would probably crack or decompose to intermediate compounds (including a char and H_2O). Therefore, it was decided to compare the decomposition products obtained from aliquots of the same material by these two techniques.

The first aliquot was placed into a capillary and sealed under vacuum. The vacuum-sealed capillary was heated at 600°C for a period of 2 hr with one end of the capillary remaining outside the heating unit to serve as a condenser. A small amount of yellow liquid was condensed at the cool end while a substantial quantity of black residue (probably carbon) formed at the original sample site. No attempt was made to obtain an infrared spectrum of this material because the sample was of insufficient quantity. Since the decomposition product was obviously not normal water, a freezing point determination was not made. These results seem to indicate that the sample was partially organic. The infrared spectrum of the distillate suggested that borates may also be present.

The second aliquot was heated at 600°C for 2 hr but in air. It was thereby hoped to decompose the sample into $CO_2 + H_2O$. A clear liquid formed at the cool end of the capillary which appeared to be H_2O. However, the liquid was found to freeze at -4°C which could mean that it contained some solute, e.g., borate. In addition to this liquid, some carbon was found on the walls of the capillary similar to that found in the evacuated sample, although a much smaller quantity.

The general conclusions from these decomposition experiments are:

1. The particular distillate is predominantly organic in nature.

2. The decomposition is not quite identical to that reported earlier or to the Russian work. Thus in presence of air, H_2O is not the only visible product.

Distillation of Sodium Tetraborate and Boric Acid: Since the presence of a tetraborate was positively identified by IR, in the residue from polywater distillation no. 5 and strongly suggested in the distillate itself (refer to Figs. 11 and 12), it was decided to attempt a direct distillation of $Na_2B_4O_7$.

Sodium tetraborate (Baker Analyzed Reagent grade) was placed in distillation chamber D (not under vacuum) and the heating unit was heated gradually. No product was observed at 100, 150, 200, 250, 300 and 450°C; only water condensation was found at the cool end of the tube. Then HCl was added to $Na_2B_4O_7$, to form H_3BO_3. The IR spectrum of this boric acid is shown in Fig. 13. This material was successfully distilled at 150°C, and the infrared absorption of this distillate was identical to that of the starting material. An interesting feature of this spectrum is the absence of any absorption at 1000 cm^{-1}, which has always been observed for the tetraborate. The fact that boric acid distills, and absorbs at 1400 cm^{-1} makes it not improbable that distillation product no. 5 does contain some of this material.

These two distillations were repeated under vacuum, with essentially the same results; the tetraborate salt would not distill and the boric acid distilled completely at the low temperature of 100°C.

Distillation no. 6: This experiment was performed on Pyrex-grown material which was air dried at 200°C for 2 hr prior to distillation at 300°C in vacuum. A yellow liquid condensed over. The condensate was then decomposed at 600°C in the same chamber. Part of the condensate carbonized and the rest of the sample condensed at the cool end of the chamber as a clear liquid (possibly H_2O). When this liquid was redistilled back to the carbon component, in turned yellow, probably as a result of extracting material, not completely decomposed, from the carbon layer. Fig. 14 shows the decomposition products. An infrared spectrum of this yellow liquid displayed no IR activity.

Distillation no. 7: This is the only distillation experiment, to date, for which zirconia-grown material was used. This may also be the purest material to be distilled, since absence of borates is assured. It was decided to distill the sample fractionally in 100°C increments in an attempt to separate the different components.

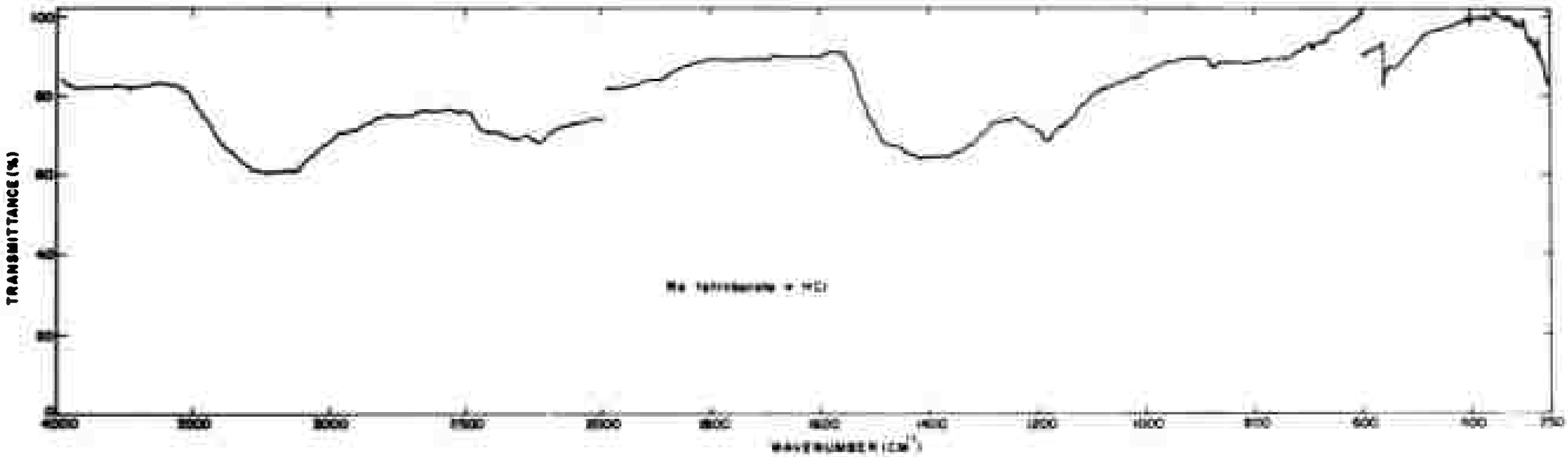


Fig. 13. IR spectrum of acidified $Na_2B_4O_7$

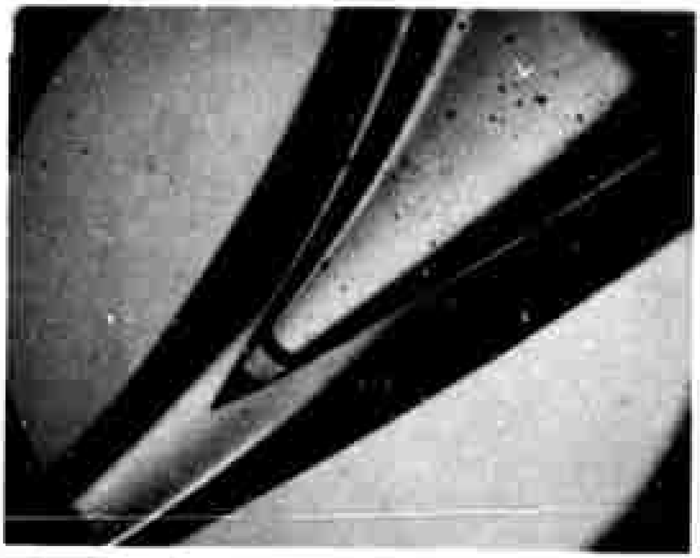


Fig. 14. The decomposition products from distillation no. 6

The first step of the distillation was carried out at 100°C. It produced first a clear and then a yellow liquid. The residue was then removed and put into a new chamber, and the experiment repeated at 200°C. A yellow distillate was also formed. The experiment at 300°C yielded 32×10^{-3} $\mu\ell$ of dark yellow distillate. This produce appeared powdery while the 200°C product seemed oily. The 400°C product was a brownish powder distillate which was of much smaller volume than the other distillates. The residue became black during this experiment. At 500°C, very little distillate formed and the experiment was terminated.

Infrared analysis was then attempted on all the distillation fractions and on the residue. The 100°C fraction showed no IR activity and was probably composed mostly of water. The 200°C distillate was not water soluble but when dissolved in a mixture of 75% EtOH and 25% H_2O, a weak diffuse spectrum was observed with no pronounced peaks. A slight dip in the region 1400 cm^{-1} to 1600 cm^{-1} was observed.

The 300°C product was dissolved in H_2O with difficulty and showed a well resolved spectrum (Fig 15). The spectrum was relatable to, but distinctly different from, the spectrum of the original zirconia-formed sample (Fig. 16).

The 400°C and 500°C distillates were dissolved with difficulty in H_2O but displayed no IR activity, probably because of insufficient material.

As mentioned above, the residue turned black at 400°C. It was extracted with water to separate it from the insoluble carbon component. The spectrum shown in Fig. 17 revealed that it had strong ionic carbonate peaks at 1430 cm^{-1} and 880 cm^{-1}. An additional strong peak was evident at 1000 cm^{-1}, which has not yet been identified. Since there were no carbonate peaks in the spectrum of the original zirconia-formed sample, the carbonate peaks in the residue prove conclusively that organic material must have been present in the original sample.

We have made arrangements with Dr. David Dolphin of Harvard University to collaborate with us on mass spectrometric identification of some of these stable organic components of anomalous water. The results of these experiments are discussed in Section V. Whether or not this material, is identical tc USSR-grown material is a crucial question. More generally, the identity of such highly stable and oxidation resistant compounds is of great interest.

Distillation of Poly-D_2O: We have already indicated that "poly-D_2O" and "poly-H_2O" appear identical. Working on the assumption that the only material which could possibly be a polymer of water was the water-soluble distillate, an attempt was made to distill poly-D_2O with the aim of carrying out an IR-analysis of the distillate.

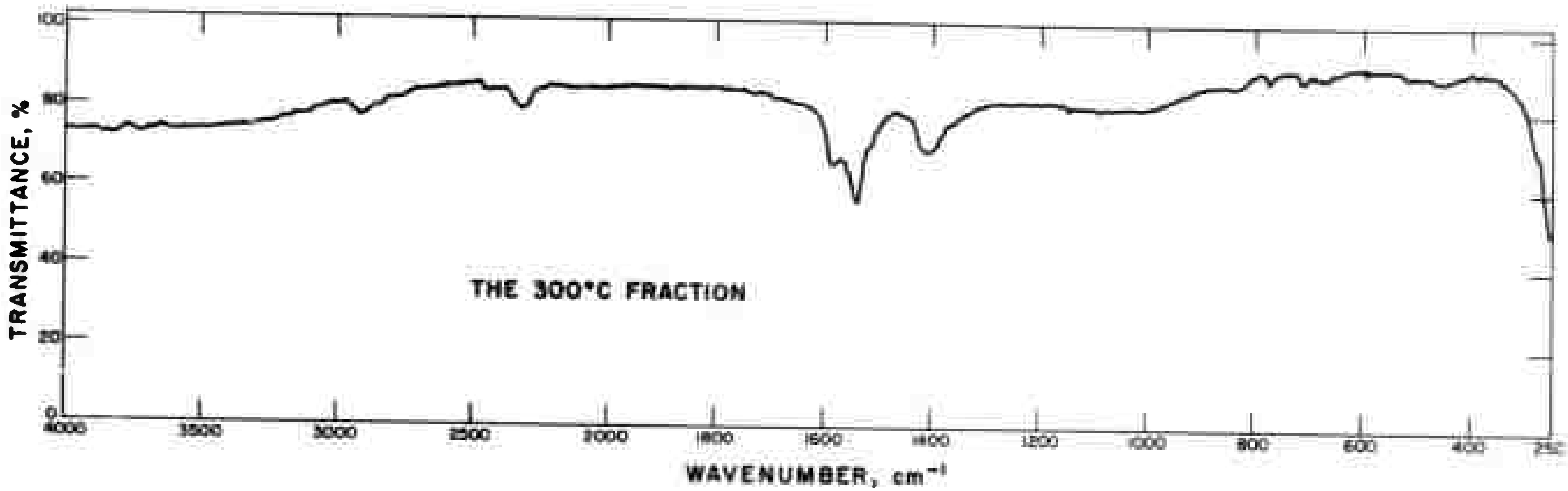


Fig. 15. IR spectrum of 300°C distillate fraction of zirconia produced anomolous water

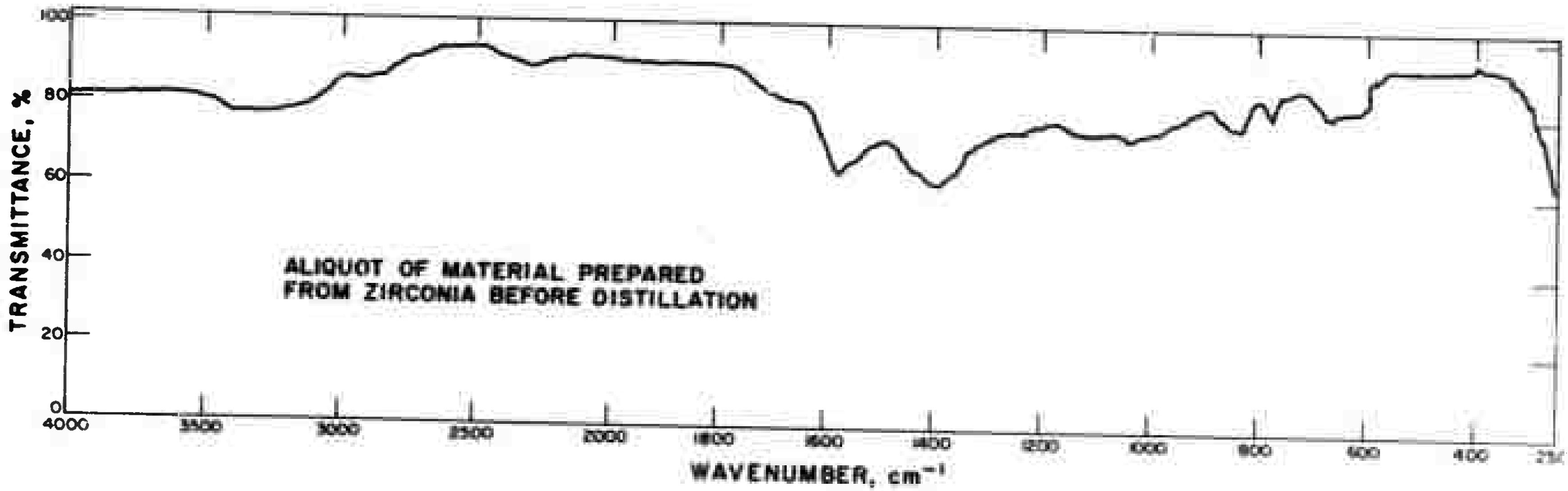


Fig. 16. IR spectrum of zirconia produced anomolous water

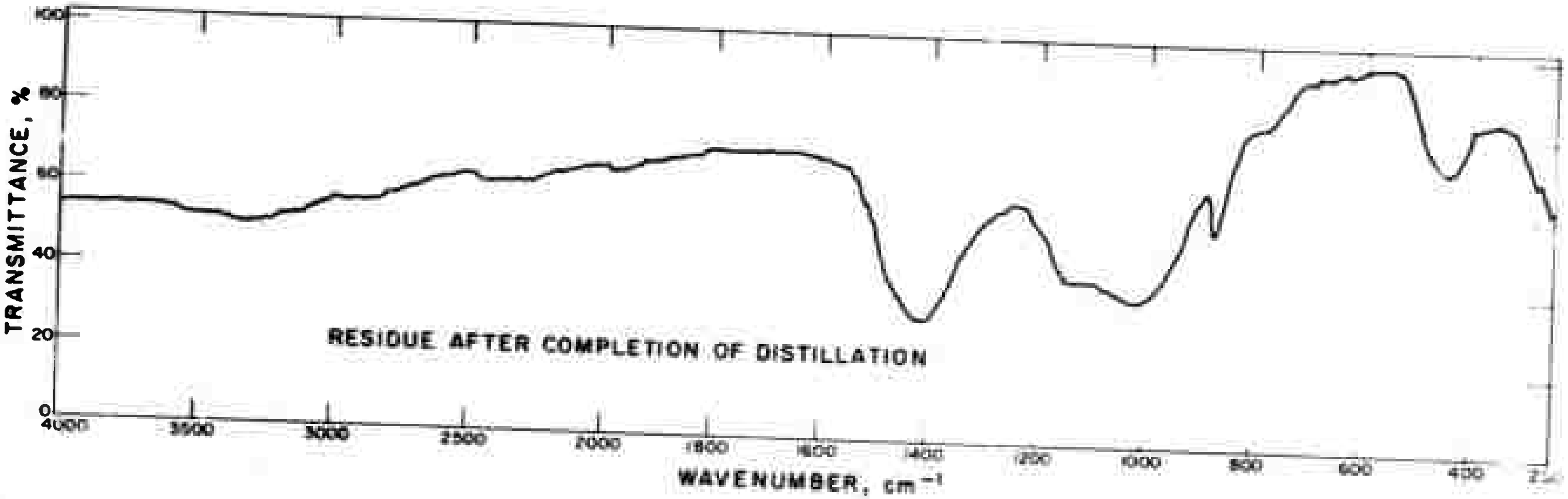


Fig. 17 IR spectrum of distillation residue of zirconia produced material

The sample for distillation was prepared from Pyrex cones suspended over a solution of D_2O under vacuum. All extracting and other handling was carried out in a glove bag continually flushed with dry N_2. The dried sample was evacuated, sealed and distilled at 300°C.

The distillate was yellow and oily in appearance and proved to be insoluble in D_2O. This property made infrared analysis impractical since transferral of such a small quantity of material to an AgBr plate can only can only be accomplished by first dissolving the sample in hydrogen free solvent.

Since the type of experiment which might be performed on this distillate was limited by the fact that the material would not dissolve in D_2O, it was decided to attempt a decomposition at 600°C in a vacuum. The results of this experiment were, predictably, much the same as in the case of the 300°C distillation. The major portion condensed at the cool end of the chamber as a dark yellow material which also proved to be insoluble in D_2O; a small amount of the sample remained behind and decomposed to a black char.

The evidence from these experiments indicates quite strongly that the sample is principally organic in nature.

V. REFRACTIVE INDEX AND MASS SPECTRUM OF ANOMALOUS WATER

During this period, techniques for measuring the refractive index of microgram quantities of material were mastered. Our method is based on that described by Deryagin.[5] Fig. 18 shows the apparatus. The light source at the focal point of the lens produces a parallel beam of light which impinges onto a capillary immersed in a fluid. Since the index of refraction of this liquid is matched to that of the capillary, the parallel beam of light is not bent by the capillary walls. However, the contents of the capillary, which have a different index of refraction, act as a cylindrical lens, and bring the light to focus at a focal line. This line is above the axis of the capillary if the sample index is greater than that of the container walls and below the axis if the index is less. In the cases of anomalous water, normal water, and air, the refractive indices are all smaller than that of the capillary. Therefore, these samples act as diverging lenses and the focal line is located below the capillary. A 32X microscope objective is used to view the capillary and the line images. By using a green filter, the chromatic aberation is reduced and the focus was made sharper.

The measurement is carried out with a sealed capillary, partially filled with the sample. The meniscus of the sample is placed in the center of the field so that one side of the field contains the sample filled portion of the capillary while the other side contains the air column portion. After the capillary itself is brought into focus, the stage is raised until the air column side displays a bright line. The stage is then raised further until the sample side of the capillary is bright. By using the calibrated drum of the microscope stage focusing mechanism, the distance between the focal line of the sample and the focal line of the air can be measured. Fig. 19 shows the capillary with the air focal line in focus.

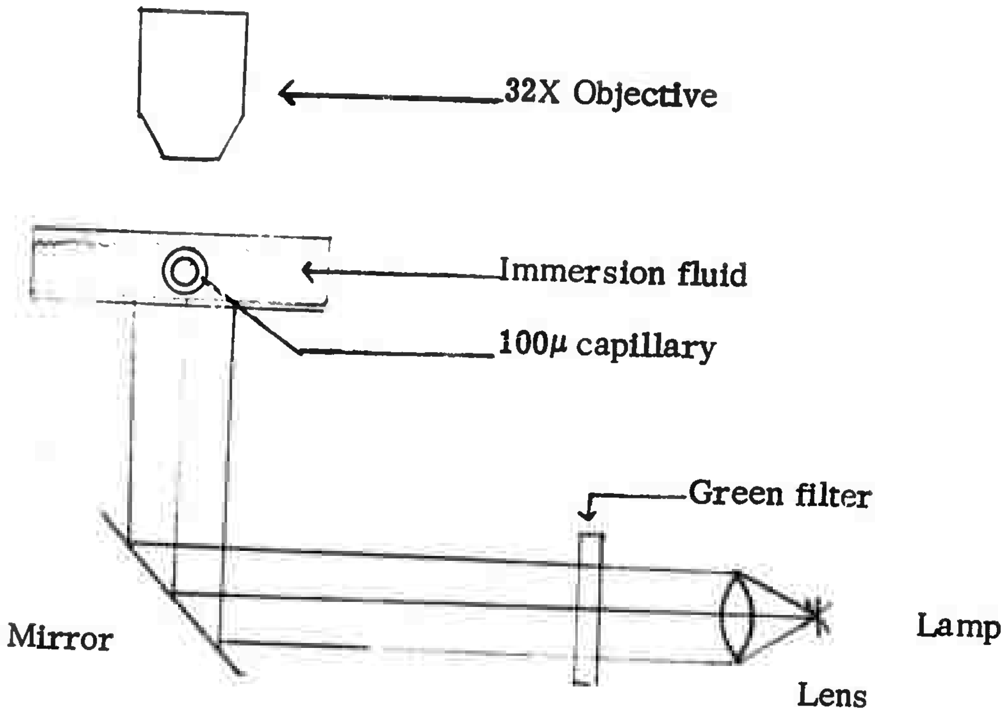


Fig. 18. Apparatus for measuring the refractive index of small samples

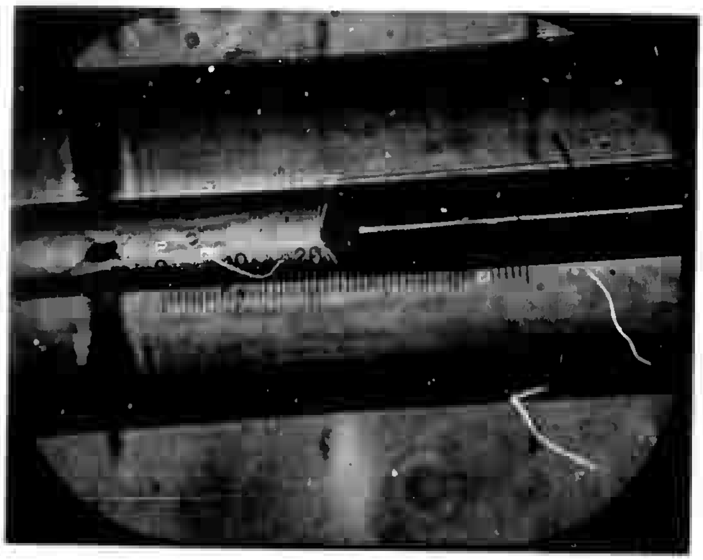


Fig. 19. Focal line of air in capillary acting as a cylindrical lens

This difference in focal length can be shown to be:[5]

$$\Delta f = f_{air} - f_{sample} = dn_c \ (n-1)/4 \, (n_c-1) \ (n-n_c) \qquad (1)$$

where

d = capillary inner diameter
n_c = index of refraction of capillary and the immersion oil
n = index of refraction of sample.

Although n can be calculated from this formula, it was felt to be advantageous to calibrate the measurement using solutions of known indices of refraction and to use these empirical data to determine the index of the sample.

With our initial procedures, it was found that the $\Delta f/d$ readings were severely displaced from theoretical values. It also appeared that $\Delta f/d$ may not be truly independent of capillary inside diameter, and with the wide variation normally experienced in capillary diameters (± 10% for quartz), the precision of the measurements was jeopardized.

However, it was discovered that precision could be improved immensely with the use of an immersible objective for the viewing microscope lens. Using such a lens eliminates the extra bend of the light beam as it passes from the immersion fluid into the air above it. This bending causes the capillary to appear nearer to the fluid surface than it actually is, an effect quite dependent on capillary diameter and depth of fluid. This improvement in technique also allowed us to observe $\Delta f/d$ values much closer to theoretical values, as is evident in Figs. 20 and 21. Fig. 21 is the standard curve obtained using precision bore Pyrex capillaries which have a variation in i.d. of only ± 2.5% (hand blown capillaries have ± 10%).

With the use of the immersible lens and with refined diameter measuring techniques, a precision of 0.5% on the refractive index measurement can be obtained despite 30% variations in capillary size. This allows us to calculate the refractive index of undiluted anomalous water to within 0.01.

The refractive index of pure anomalous water residue is difficult to measure directly. This is because the residue contains bubbles and scatters light so much that no focal line can be observed. Therefore, solutions of anomalous water were measured and the required result obtained by extrapolating to zero dilution. The standard method for such determination is as follows:

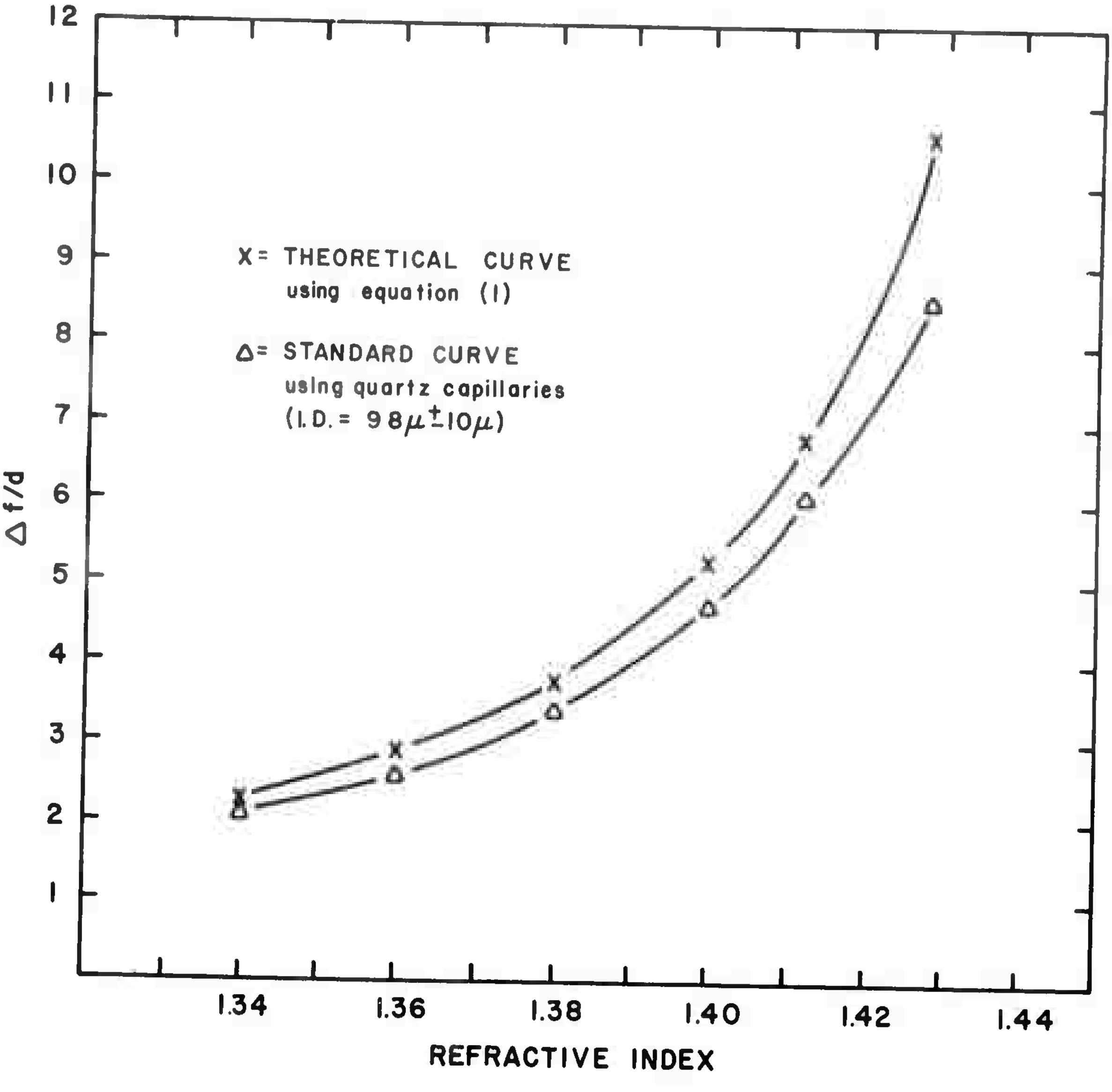


Fig. 20. Dependence of Δ f/d as a function of n obtained with a set of standard refractive index solutions in quartz capillaries

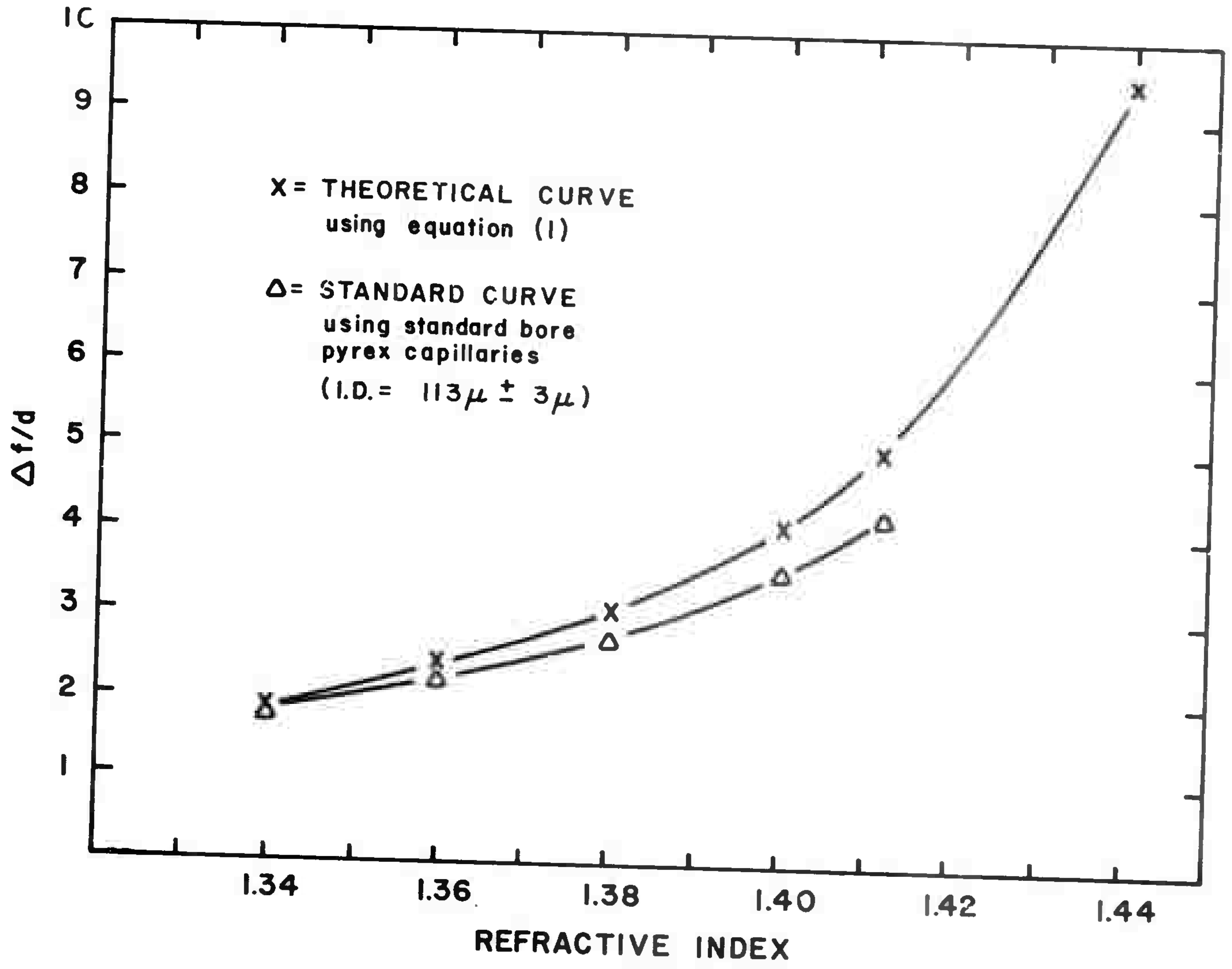


Fig. 21. Dependence of Δ f/d as a function of n obtained with a set of standard refractive index solutions in Pyrex capillaries

The molar refraction R_{12} of a two component solution is given by:

$$R_{12} = \frac{X_1 M_1 + X_2 M_2}{\rho} \cdot \frac{n^2-1}{n^2+2} \qquad (2)$$

Here is the refractive index of the solution, X_i and M_i $/n^2-1/n^2+2/$ the mole fractions and molecular weights of the constituents, and ρ the solution density. R_{12} is also known to be the sum of the contributions from each of the constituents:

$$R_{12} = X_1 R_1 + X_2 R_2 \qquad (3)$$

where

$$R_i = \frac{n_i^2-1}{n_i^2+2} \cdot \frac{M_1}{\rho_1} \qquad (4)$$

Then, we equate (2) and (3), we recall that for a column of polywater ℓ_o long at humidity such that $\ell = r \cdot \ell_o$

$$\rho = \frac{1.4\,\ell_o + (\ell - \ell_o)}{\ell} = \frac{r + 0.4}{r}, \qquad (5)$$

and note that the mole fractions of the components are defined by

$$X_{H_2O} = \frac{\frac{\ell - \ell_o}{18}}{\frac{\ell - \ell_o}{18} + \frac{\ell_o (1.4)}{M_{pw}}} = \frac{r - 1}{(r - 1) + 25.2/M_{pw}}, \qquad (6a)$$

$$X_{pw} = \frac{25.2/M_{pw}}{(r - 1) + 25.2/M_{pw}} \qquad (6b)$$

Then, since $n_{H_2O} = 1.33$, we obtain the expression

$$\frac{n_{pw}^2 - 1}{n_{pw}^2 + 2} = \frac{n^2 - 1}{n^2 + 2} + 0.206. \qquad (7)$$

Thus, n_{pw} can be obtained from refraction measurements on any solution of known composition.

Table I shows the application of this formula to our measurements. As a test of both the experimental technique and method of calculation, samples of NaCl and glycerin were prepared and the refractive indices measured. The validity of the system was proven with observed values within 0.3% for glycerine and 2% for NaCl.

The values for polywater, on the other hand, cover a rather wide range. It should be noted that the accuracy of these determinations relies heavily on the accuracy of the ℓ_o measurement. This measurement can be read to within ± 0.0001 in. However, it is important that the dry column to be measured be dense and compact, otherwise the error in the measurement would rise significantly. An equally important factor in this regard is the relative amount of material present in the capillary. Referring to Table I, one sees that in the case of the quartz-grown material, the sample length was only 0.0016-in. and therefore the error in this reading can be greater than 10%. This is undoubtedly reflected in the wide variation in the calculated values for refractive index.

For future determinations, this source of error will be minimized by preparing samples with dry column lengths of ~ 0.01-in. so that the error in ℓ/ℓ_o would be no greater than 2%. Another way of obtaining an accurate ℓ_o would be to measure the length of the column as a function of humidity (R) and to extrapolate the plot of R/1-R versus ℓ to zero humidity.

Comparison between our results (Table I) and those of the Russians can be made only in a general fashion and it is clear that the materials are similar. It is not known how much scatter they observed in their results since they did not correlate the refractive index with dilution factor; they reported data for material in the range of 1.33 (normal water) to 1.49 (maximally modified water). If the scatter in our results persists after minimizing the error in ℓ_o, we would have to assume that we are dealing with a mixture of materials and not a pure compound.

In the hope of identifying some of the more stable organic components of polywater, mass spectroscopy experiments were carried out on various samples. These experiments were performed in collaboration with Dr. David Dolphin of Harvard University.

Samples were placed on a ceramic holder, previously flamed clean, which was placed in the spectrometer. The chamber was then pumped to 10^{-9} mm of Hg. In order to obtain greater peak heights, several (up to five) aliquots of material were

Table I. Refractive Index Measurements

	Sample	ℓ_o	ℓ	ℓ/ℓ_o	$\Delta f/d$	Refractive Index From Graph	Refractive Index At Zero Dilution	Refractive Index Theoretical
No. 1	Quartz grown	0.0016	0.037	23.13	1.99	1.33	1.25 ± 0.15*	
	Quartz grown	0.0016	0.0039	2.438	2.539	1.3585	1.39 ± 0.17	
No. 1	Zirconia grown	0.0055	0.025	4.545	3.102	1.373	1.52 ± 0.06	
	Zirconia grown	0.0050	0.0128	2.56	2.19	1.3422	1.35 ± 0.05	
No. 2	Zirconia grown	0.0090	0.0222	2.46	3.14	1.3735	1.43 ± 0.03	
No. 1	Pyrex grown	0.0305	0.0802	2.63	2.83	1.365	1.42 ± 0.01	
	10% NaCl	4.619	95.38	20.65	2.163	1.342	1.510	1.544
	Glycerin	0.794	2.79[illegible]	3.52	2.964	1.37	1.467	1.472
	Glycerin	0.794	1.794	2.259	3.954	1.39	1.464	1.472

* These error limits are based on the precision of reading ℓ_o; they do not take into account the uncertainty from the possibility that the dried material is not 100% dense, nor other reading errors (e.g., in ℓ).

deposited on to the holder with rough pumping between each, in order to evacuate the material to dryness.

The first set of measurements was made at temperatures ranging between 220°C and 350°C, using as-grown Pyrex material taken from the 1 mg sample previously amassed. The results of the measurement at the various temperatures are shown in Table II. The largest peaks at the lowest temperature (220°C) were at 60 and 149 mass numbers [the peaks at 28 (N_2) and 44 (CO_2) were also present in the blank]. As the temperature was raised, the peak at 149 disappeared (above 270°C), while the peak at 60 continued to increase in size until 305°C. This may indicate that the latter is a decomposition product of the former. At higher temperatures, we begin to see a peak at 207. Other peaks at 85 and 139 also appear at elevated temperatures, in addition to more CO_2 and N_2 than can be explained by what was found on the blank. However, it is not certain that these did not result from residual material from other experiments, which was not removed from the vacuum chamber of the instrument when cleaned.

The results for a second sample are also displayed in Table II. The results are comparable with those of the first sample. Both results indicate that the 149 MW species is volatile at lower temperatures and it was decided that a second series of measurements should be made at temperatures below 220°C.

Table III shows the results of the second set of experiments. The Pyrex-grown sample was taken from the same source as in the previous experiment, namely the 1 mg sample. The component with mass number 149 showed increasing peak height with temperatures in the range used; 80°-125°C. An additional component was observed at mass number 73. In the previous experiments this peak was not monitored since it was also quite strong in the background runs. As was expected, the 207 component was not observed at these lower temperatures.

The next sample to be tested was zirconia-grown material. All the mass numbers observed with the Pyrex-grown polywater were observed with this sample as well with one additional component occurring at mass number 87-88. This was a relatively strong peak with maximum height at about 280°C. The more prominent components are depicted in Fig. 22 in the form of peak height versus temperature.

The last sample to be tested was the 300°C fraction from the distillate of zirconia-grown material (distillation no. 7). Since the sample size was small, the peaks were all somewhat weak. However, it should be noted that the components with lower mass number are of about equal intensity as the heavier components; whereas

Table II. Peak Heights for Samples Taken from Pyrex 1-mg Preparation

Sample	Temperature of Sample	Mass Number							
		29 (28)	45 (44)	60	69	85	139	149	207
Blank	220	1.0	1.6	0.8	5.8	6.7	-	0.5	-
First Sample	220	0.6	1.2	2.0	1.7	0.3	-	1.0	-
	255	0.9	1.5	1.7	1.6	0.4	-	0.3	-
	270	4.9	5.8	6.8	1.7	0.9	0.4	0.4	0.5
	305-320	10.5	7.4	6.2	3.3	3.7	2.6	-	0.9
	350	6.6	3.9	2.3	3.7	10.8	2.5	-	2.6
Second Sample	220	1.2	3.4	2.2	3.3	0.7	-	6.4	-
	280	1.6	2.2	2.2	2.7	2.2	1.1	0.35	0.5
Blank	340	4.0	0.4	<0.3	1.2	4.6	-	-	1.9

Table III. Peak Heights for Three Samples

Sample	Temperature of Sample Probe, °C	Mass number 45	60	73	87	88	139	149	207
Blank	60	–	–	–	–	–	–	–	–
Background	70	2.8	0.6	0.7	–	–	0.7	1.0	–
Pyrex	80	4.0	2.4	1.4	–	–	1.8	1.4	–
Pyrex	125	~ 4.8	3.1	1.5	–	–	1.7	1.7	–
Background	125	1.8	0.9	0.8	–	–	1.0	0.8	–
Background	40	~ 12	0.9	–	–	–	–	0.4	–
Zirconia	110	~ 4.8	2.9	–	–	–	1.5	1.4	–
Zirconia	175	~ 5.6	4.5	–	–	–	1.2	1.5	–
Zirconia	235	~ 8	~ 6.4	~ 4.8	4.0	~ 4.5	0.9	2.5	0.9
Zirconia	260	~10.4	~ 10.4	~ 6.4	~ 6.4	~ 4.8	1.1	1.1	1.4
Background	275	3.3	1.7	–	--	–	1.3	0.8	–
Zirconia	280	~10.4	~ 12.8	~ 8	~ 5.6	~ 5.2	1.4	1.2	2.6
Zirconia	290	~ 8	~ 16	~ 8	3.1	3.2	1.7	1.0	2.0
Background	290	2.5	1.5	1.5	–	–	1.4	0.8	0.8
Zirconia 300° distillate	235	4	1.0	1.1	–	–	1.0	1.2	–
Zirconia 300° distillate	275	2	1.2	1.1	–	–	1.0	1.1	–
Zirconia 300° distillate	290	2.6	1.1	1.1	–	–	1.1	0.9	0.7

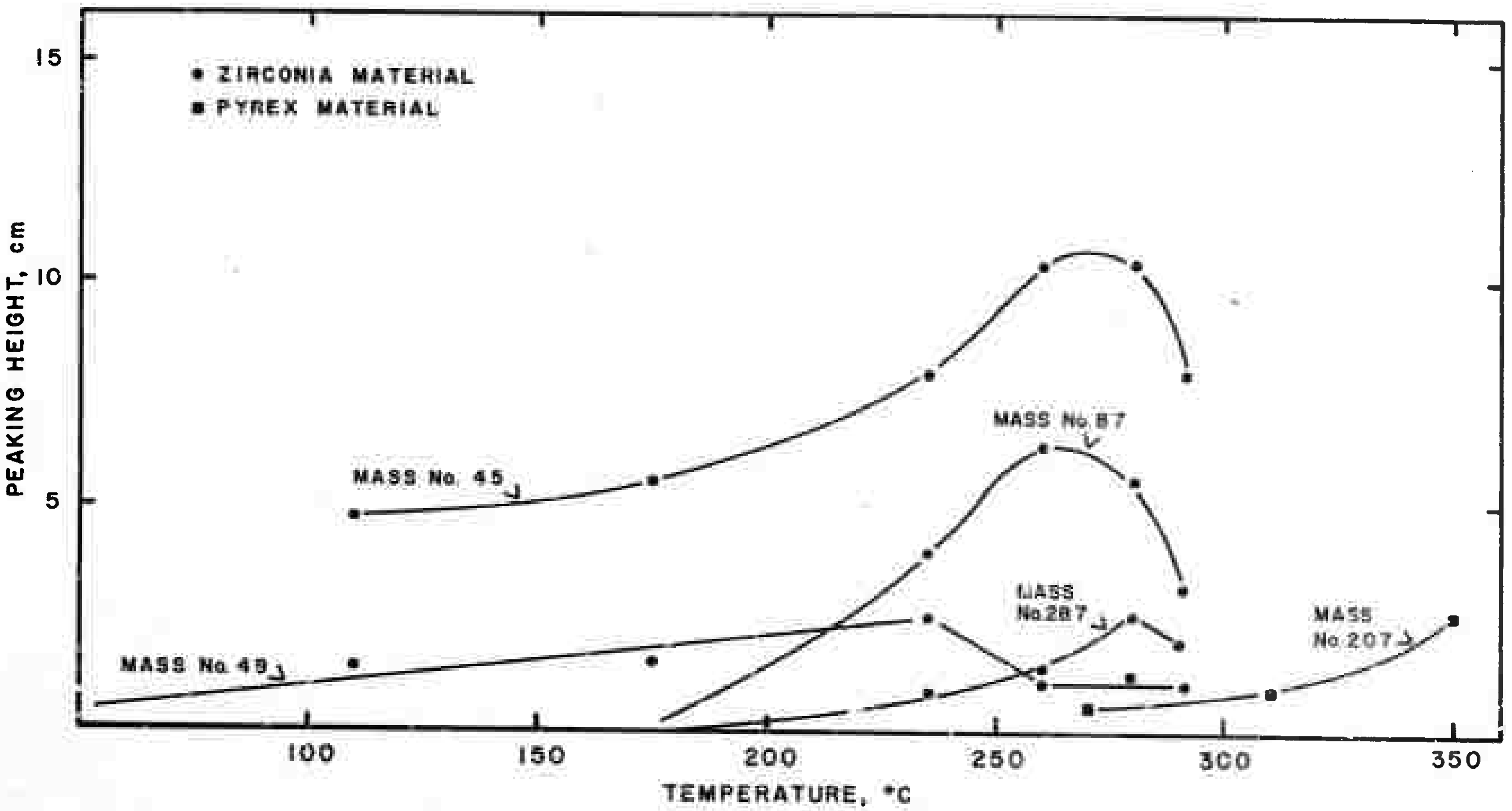


Fig. 22. Peak height versus temperature for various mass numbers

in the previous experiments, the 45 (CO_2), 60, and 73 portions were much stronger than the 149 and 207 mass numbers. This would imply that this material is of highest molecular weight and has greater stability than the original material which would be consistant with its mode of preparation.

We would conclude from these experiments that we are preparing essentially the same material on both Pyrex and zirconia glass and that the molecular weight of the material is 207.* It is also apparent that none of the prominent mass numbers observed could be caused by a polymeric form of water.

Additional mass-spectrometric work will be performed to include measurements on quartz-grown polywater and heated sodium lactate. If polywater is, in fact, a combination of carboxylic acids, there should be a reoccurrence of the mass numbers noted here when observing the cracking components from the lactate.

---

* This is in reasonable agreement with our previous estimate[24] for the MW of ~ 250. It would imply that the density value (1.4) used in that calculation is too high; based on these data, a value of ~ 1.16 would appear more appropriate.

VI. SUMMARY AND FURTHER WORK

Results in the present period confirm the organic origin of the IR-active component of anomalous water and make it more likely that this material is identical to that in the Russian literature. Two final objectives will be sought in our further work:

1. To tie-up conclusively our material with U.S.S.R. - grown material.
2. To identify and, if possible, synthesize the stable organic components of anomalous water.

Item (1.) will be addressed through the following experiments:

a. Further studies will be made of refractive index.

b. Attempts will be made to synthesize quartz-grown anomalous water under so-called "organic-free" conditions.[2] Thus, the Russians reported that their quartz capillaries were baked in vacuum at 400°C for 2 days before exposure to water vapor. They evidently believe that organic compounds would not survive this procedure. They may be the case, but our distillation results, for example, suggest otherwise.

c. Russian data suggest that "maximally modified anomalous water" boils at ~ 300°C;[28] our material is much less volatile. If our theory that anomalous water is the salt of an organic acid is correct, this difference may result from a systematic difference in acidity in the preparative techniques - ours being the more alkaline. It is proposed, then, to distill our material from acid (probably H_3PO_4). Then, we will estimate the boiling of the high boiling components by evaporation into a capillary of known size.

To determine the identity of the organic components of our material, the following experiments are intended:

a. Further mass spectroscopy of various samples.

b. Study of the product of heating Na lactate by mass spectroscopy, C-H annalysis and nmr.

VII. REFERENCES

1. N.N. Fedyakin, Kolloid Zhur., 24, 497 (1962).
2. B.V. Deryagin and N.V. Churaev, paper presented at Lehigh University conference of "Anomalous Water," June 1970. J. Colloid and Interface Sci., 36, 415 (1971).
3. B.V. Deryagin, N.V. Churaev, N.N. Fedyakin, M.V. Talaev and I.G. Ershova, Izv. Akad. Nauk SSSR, Ser. Khim., 1278 (1967).
4. B.V. Deryagin, D.S. Lychnikov, K.M. Merzhanov, Ya.I. Rabinovich and N.V. Churaev, Dokl. Akad. Nauk SSSR, 181, 823 (1968).
5. B.V. Deryagin, Z.M. Zorin and N.V. Churaev, Dokl. Akad. Nauk SSSR, 182, 811 (1968).
6. B.V. Deryagin, B.V. Zhelezny, Ya.I. Rabinovich, V.K. Simonova, M.V. Talaev and N.V. Churaev, Dokl. Akad. Nauk SSSR, 190, 372 (1970).
7. B.V. Deryagin, Z.M. Zorin, V.V. Karasev, V.D. Sobolev, E.N. Khronova and N.V. Churaev, Dokl. Akad. Nauk. SSSR, 187, 605 (1969).
8. B.V. Deryagin, Z.M. Zorin, Ya.I. Rabinovich, M.V. Talaev and N.V. Churaev, Dokl. Akad. Nauk SSSR, 191, 859 (1970).
9. E. Willis, G.K. Rennie, C. Smart and B.A. Pethica, Nature, 222, 159 (1969).
10. S.B. Brummer, F.H. Cocks, G. Entine and J.I. Bradspies, paper presented at Lehigh University conference on "Anomalous Water," J. Colloid and Interface Sci., 36, 489 (1971).
11. B. Fabuss, paper presented at Lehigh University conference on "Anomalous Water," June 1970; report on contract 14-01-0001-2096, R & D Progress Report No. 558, published by Office of Saline Water, Department of the Interior.
12. G.A. Castellion, D.G. Grabar, J. Hession and H. Burkhard, Science, 167, 865 (1970).

13. E.R. Lippincott, R.R. Stromberg, W.H. Grant and G.L. Cessac, Science, 164, 1482 (1969).

14. D.L. Rousseau and S.P.S. Porto, Science, 167, 1715 (1970).

15. S.W. Rabideau and A.E. Florin, Science, 169, 48 (1970).

16. T.F. Page, R.J. Jakobsen, E.R. Lippincott, Science, 167, 51 (1970).

17. D.L. Rousseau, paper presented at Lehigh University conference on "Anomalous Water," June 1970; J. Colloid and Interface Sci., 36, 434 (1971).

18. L.E. Davis, D.L. Rousseau, and R.D. Board, Science, 171, 167 (1971).

19. D.L. Rousseau, Science, 171, 170 (1971).

20. A report on the data of V.L. Talroze is given by V. Zhvirblis, in Khim. Zhizn, 5, 37 (1969).

21. V.V. Karazev, Yu.M. Luzhuov, J. Phys. Chem. (USSR) 42, 2366 (1968).

22. L.J. Bellamy, private communication.

23. T.F. Page and R.J. Jakobsen, paper presented at Lehigh University conference on "Anomalous Water," June 1970; J. Colloid and Interface Sci., 36, 427 (1971).

24. S.B. Brummer, J.I. Bradspies, C. Leung, H. Lingertat, and G. Entine, Final Report on Contract 14-01-0001-2259, December 1971.

25. S.B. Brummer and G. Entine, Final Report on Contract DAAH01-70-C-1006, May 1971.

26. N.N. Fedyakin, B.V. Deryagin, A.V. Novikova and M.V. Talaev, Dokl. Akad. Nauk SSSR, 165, 878 (1965).

27. S. Glasstone "Physical Chemistry," 2nd Ed., N.Y., 528-532, 1946.

28. B.V. Deryagin, N.V. Churaev, Ya.I. Rabinovich, O.A. Kiseleva, S.P. Vnukov, Dokl. Akad. Nauk SSSR, 195, 398 (1970).